EXPERIMENTAL INVESTIGATION OF LOW SALINITY ENHANCE OIL RECOVERY POTENTIAL AND WETTABILITY CHARACTERIZATION OF ALASKA NORTH SLOPE CORES

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A

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ABSTRACT

Rock wettability and the chemical properties of the injection water influence fluid distribution and multiphase fluid flow behavior in petroleum reservoirs and hence it consequently affects the final residual oil saturation. Many researchers have proven that oil recovery is increased by decreasing the salinity of water used for waterflooding process.

Three sets of experiments were conducted on representative Alaska North Slope (ANS) core samples to experimentally ascertain the influence of injected brine/fluid composition on wettability and hence on oil recovery in secondary oil recovery mode. All the sets of experiments examined the effect of brine salinity variation on wettability and residual oil saturation of representative core samples. The core samples used in the first and third set were new (clean) while in the second set core samples were oil aged. For first and second sets laboratory reconstituted 22,000 TDS, 11,000 TDS and 5,500 TDS (total dissolved solids) brines were used while for the third set ANS lake water was used.

Oil aging of core decreased the water wetting state of cores slightly. This observation could be attributed to adsorption of polar compounds of crude oil. The general trend observed in all the coreflood experiment was reduction in S_{or} (up to 20%) and slight increase in the Amott-Harvey Wettability Index with decrease in salinity of the injected brine at reservoir temperature.

DISCLAIMER

The material was prepared with financial support from the Arctic Energy Technology Development Laboratory, US Department of Energy. Their support is highly appreciated. The opinions, findings, conclusions, and recommendations expressed herein are those of the author and do not necessarily reflect the views of the US Department of Energy. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof.

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CHAPTER 1
INTRODUCTION

1.1 Background

Oil exists in subterranean formations or reservoirs in a wide variety of forms, in a wide variety of formations and under a wide variety of natural conditions. In most cases natural forces present in the reservoir permit the production of significant amounts of the oil by primary recovery methods. Usually this is brought about by the fact that reservoir pressure, supplied by gas under pressure, either present in the oil or as a gas cap, water, etc. is sufficient to force the oil to the surface. In any event, these primary recovery methods are capable of recovering limited volumes of the original oil in place due to depletion of the natural forces and other factors. In some cases, little or none of the oil can be produced by natural forces. Accordingly, a wide variety of supplemental or artificial recovery techniques are employed and new methods are being proposed in order to increase the recovery of oil from subterranean formations or reservoirs. If the artificial recovery technique is utilized in reservoirs after primary recovery then this production technique is referred to as a secondary recovery technique. If a secondary recovery technique is followed by another artificial recovery technique, the latter is often referred to as tertiary recovery technique. "Enhanced oil recovery" technique is also one of the best terms to refer to these artificial recovery techniques.

All such enhanced oil recovery techniques include the injection of gas or water into one or more injection wells under a pressure sufficient to displace or drive at least a portion of the oil from the reservoir. It is also well known in petroleum fields to use various methods and techniques for improving oil recovery efficiency in the secondary recovery process. After reviewing laboratory studies conducted over a period of many years, oil recovery techniques like low salinity water flooding appear to be very promising for improved oil recovery (Anderson, 1986a, 1987).

Oil recovery efficiency is a function of many interacting variables / factors at pore levels as well as macroscopic scales. Among the many identified factors that affect oil recovery efficiency, the reservoir wetting state has been shown to be one of the most important. Wettability is a major factor controlling the location, flow and the distribution of fluids in a reservoir. Based on the research findings over many years on the nature of wettability, the importance of wettability in the oil recovery process has been agreed on by many researchers (Anderson, 1986a). Laboratory studies (McGuire et al., 2005; Webb et al., 2004, 2005) conducted over a period of many years have indicated that oil recovery could be improved by injecting lower salinity water. Although the recovery mechanisms are still uncertain, they appear to be similar to those found in alkaline flooding.

1.2 Wettability and Oil Recovery

Wettability is the tendency of the reservoir rock surface to preferentially contact a particular fluid in a multiphase or two-phase fluid system. Consequently, a water-wet reservoir rock will preferentially contact water; an oil-wet reservoir will preferentially contact oil; and a gas-wet reservoir will preferentially contact gas. Whether a reservoir rock is strongly water-wet or oil-wet depends on the chemical composition of the fluids resulting in the molecular attraction between the water molecules and the rock and/or the oil molecules and the rock.

Over the years the effect of wettability on oil recovery efficiency has been widely acknowledged. However, the wetting phase that will result in optimal recovery of oil is still a subject of intense research debate. Previously reported observations (Amott, 1959; Donaldson et al., 1969; Owens et al., 1971) report that optimal oil recovery is observed for water-wet, intermediate-wet and oil-wet systems. The reason for this disagreement in observed reports (Amott, 1959) is attributable to a number of varying factors like (1) difficulty in wetting state reproducibility (2) the different methods adopted for wetting state characterization (3) lack of a unified standard for coring, core handing and core storage (4) the fact that a host of other reservoir rock and fluid properties, in addition to the reservoir wetting condition, also act to influence oil recovery efficiency.

1.3 Objectives

Several EOR methods currently used in Alaska include miscible gas and waterflooding. Still, more than half of the oil reserves remain in place after completion of EOR operations in a typical reservoir. All of these methods can significantly benefit from characterization and improvement of wettability, which has a profound impact on drainage, imbibition behavior, fluid sweep and oil recovery efficiency. However, the present fundamental understanding of how mixed-wetting states impact drainage, imbibition behavior, and fluid displacement processes in oil-bearing reservoirs is extremely limited. Data on the wettability states of Alaskan reservoirs are lacking in particular, and methods for rapid characterization of mixed-wettability in the laboratory and field are unavailable. Industry production data suggest that EOR operations on ANS reservoirs can be significantly improved if a better understanding of mixed wettability and methods to alter wettability states can be developed. Therefore, characterizing the wettability states of ANS reservoirs, understanding how the injected and resident fluid composition influences wettability and oil recovery, and developing methods that fundamentally improve wettability to achieve higher recovery efficiencies is crucial (Dandekar, 2003).

Based on the aforementioned background, the overall aim of this research study is as follows-

a) In secondary oil recovery mode observe the effect of variation in the salinity of the injected brine on oil recovery and residual oil saturation of Alaska North Slope (ANS) cores.
b) Observe the effect of oil aging on the wettability of cores and consequently study the effect on oil recovery and wettability variation by changes in brine salinity.
c) Observe the effect of ANS lake water (considered as a source of low salinity water) on residual oil saturation of the cores.
d) Characterize the wettability changes / alteration, using the Amott-Harvey Wettability Index in all the above mentioned cases.

CHAPTER 2

LITERATURE REVIEW

2.1 Wettability Measurements

Wettability is usually defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. The contact angle subtended by the oil-water interface against the rock surface is the universal measure of wettability. More specifically, wettability is characterized by the water-advancing contact angle since it corresponds to the oil production scenario in the reservoir.

The quantitative methods of characterizing wettability of a porous medium are contact angle measurements, the Amott-Harvey test and the USBM test. The qualitative methods are imbibition, microscope examination, flotation, glass slide, relative permeability curves, capillarimetric method, displacement capillary pressure, permeability/saturation relationships and the reservoir logs. Quantitative methods are most widely used for laboratory measurements (Anderson, 1987).

2.1.1 Quantitative Methods

2.1.1.1 Contact Angle Method

The contact angle is the best method for measuring wettability when pure fluids and artificial cores are used. This method is also used to determine whether a crude oil can alter wettability and to examine the effects of temperature, pressure and brine chemistry on wettability.

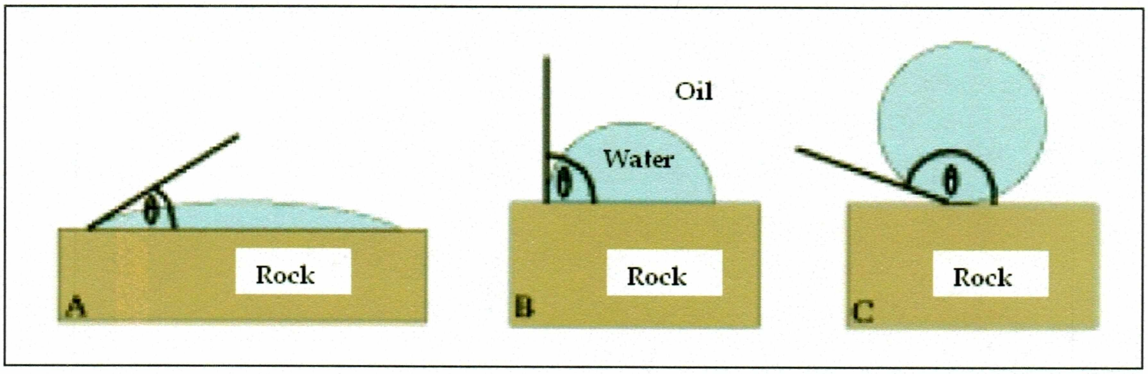

Figure 2.1 Wettability of Water-Oil-Rock System (Buckman, 2004)

Relationship between wettability and contact angle (Θ): When Θ < 90, the reservoir rock is water-wet, when Θ > 90, it is oil-wet and when Θ ≅ 90, a neutral-wet system exists (see Figure 2.1).

2.1.1.2 USBM Wettability Index

The United State Bureau of Mines (USBM) test (Donaldson, 1969) is relatively rapid which characterizes wettability by measuring the area under the curve obtained by plotting the capillary pressure against the water saturation. The USBM method uses the ratio of areas under the two capillary pressure curves to calculate the wettability index (W).

$$W = \log (A1/A2) \tag{2.1}$$

A1 and A2 are the areas under the oil and brine drive curves respectively.

When W > zero, the core is water-wet, and when W < zero, the core is oil-wet. A wettability index near zero means the core is neutrally wet. The larger the absolute value of W, the greater the wetting preference. A major advantage it has over the Amott wettability test is its sensitivity near neutral wettability.

2.1.1.3 Amott Method

The main principle of this method is that the wetting fluid will generally imbibe spontaneously into the core, displacing the non-wetting phase (Amott, 1959). The test measures the average wettability of the core using a procedure that involves five stages.

i. The test begins at residual oil saturation to waterflood, so the fluids are reduced to S_{or} (residual oil saturation) by forced displacement of brine.

ii. The core is immersed in oil for 20 hours and the amount of water displaced by spontaneous imbibition of oil, if any, is recorded as V_{wsp} (see Figure 2.2).

iii. The water is displaced to the initial water saturation by oil, and the total amount of water displaced (by imbibition and by forced displacement of oil) is recorded as V_{wtot}.

iv. The core is immersed in brine for 20 hours, and the volume of oil displaced, if any, by spontaneous imbibition of water is recorded as V_{osp} (see Figure 2.2).

v. The oil remaining in the core is displaced by water to S_{or} and the total amount of oil displaced (by imbibition and by forced displacement of water) is recorded as V_{otot}.

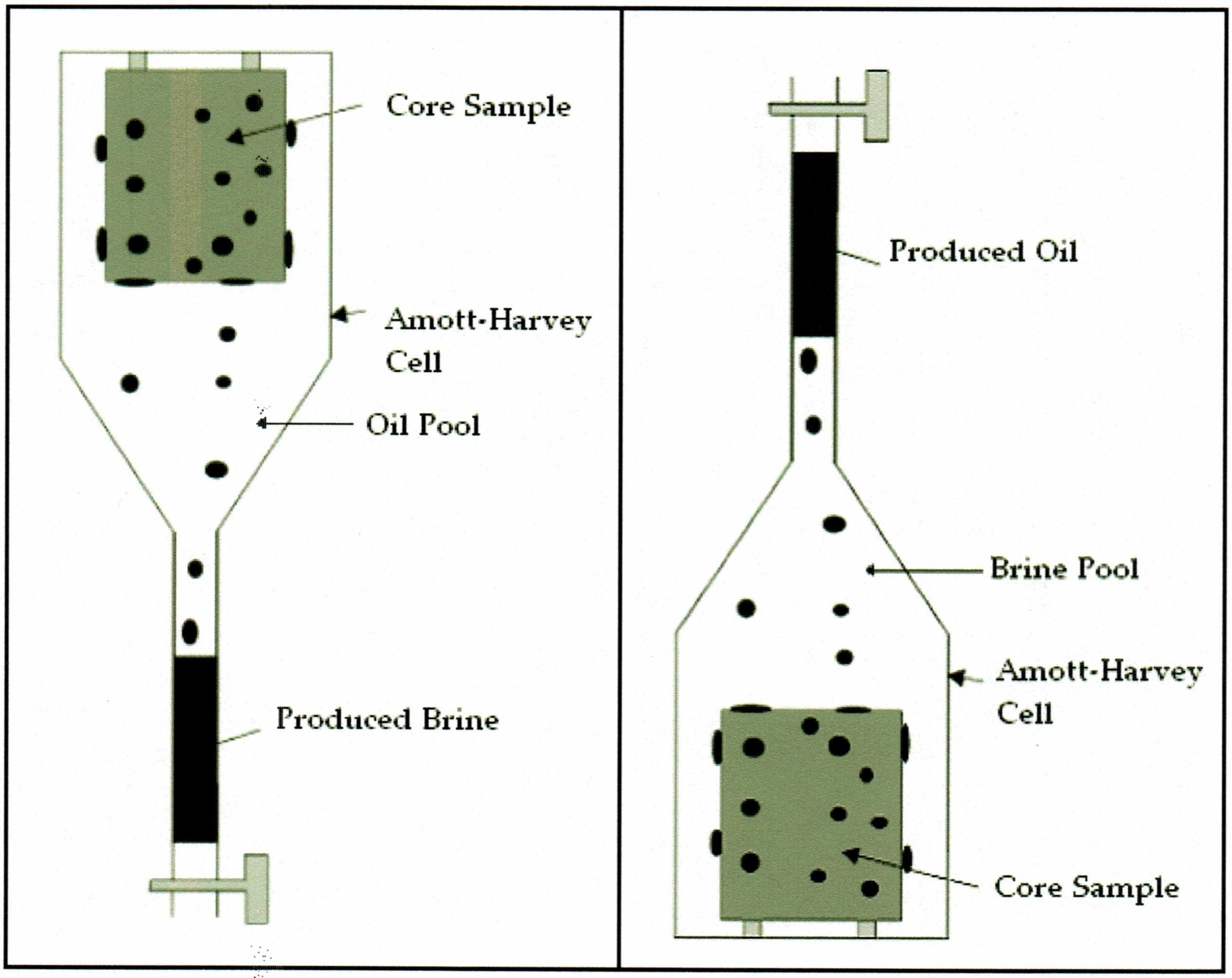

Figure 2.2 Set-up for Spontaneous Displacement of (a) Brine and (b) Oil (Modified after Karabakal et al., 2003)

The calculations are done as follows:

a) The displacement by oil ratio: the ratio of water volume displaced by spontaneous oil imbibition alone, V_{wsp} to the total displaced by oil imbibition and forced displacement V_{wtot},

$$I_o = V_{wsp} / V_{wtot} \quad \textbf{(2.2)}$$

b) The displacement by water ratio: the ratio of the oil volume displaced by spontaneous water imbibition alone, V_{osp}, to the total oil volume displaced by imbibition and forced displacement V_{otot},

$$I_w = V_{osp} / V_{otot} \tag{2.3}$$

According to Amott (1959), preferentially water-wet cores are characterized by a positive value of displacement by water ratio (I_w) and a zero value for the displacement by oil ratio (I_o). The displacement by water ratio approaches unity as the water wetness increases. Similarly, oil wet cores have a positive value of displacement by oil ratio (I_o) and a zero value for displacement by water ratio (I_w). Both the ratios are zero for neutrally wet cores indicating the absence of spontaneous imbibition of either oil or water.

A number of researchers (Boneau, 1977) used a modification of the Amott wettability test called the "Amott-Harvey relative displacement index." In the current experiments, the characterization of wettability of ANS cores is done by study of the "Amott-Harvey relative displacement index". The experimental process for both tests is the same except that the modified Amott test has an additional step in the core preparation prior to running the test. The additional step involves the saturation of the core sample with water/brine and flooding with (or centrifuged under) oil to reduce the water/brine to some initial water saturation.

The Amott–Harvey relative displacement index is the displacement by water ratio minus the displacement by oil ratio, defined as:

$$I = I_w - I_o = (V_{osp} / V_{otot}) - (V_{wsp} / V_{wtot}) \tag{2.4}$$

This combines the two ratios into a single wettability index that varies from +1 for complete water wetness to –1 for complete oil wetness with zero representing the neutral wettability. Cuiec's (1984) wettability classification based on the Amott-Harvey Index (I_{AH}) is as follows:

Table 2.1 Cuiec's Wettability Classification Based on the Amott-Harvey Wettability Index, I_{AH}, (Cuiec, 1984)

I_{AH} Range	Wettability
+0.3 to +1.0	water wet
+0.1 to +0.3	slightly water wet
–0.1 to +0.1	neutral
–0.3 to –0.1	slightly oil wet
–1.0 to –0.3	oil wet

The Amott-Harvey test measures the total volume of spontaneous and forced imbibition of oil and water. If we are able to measure the imbibition rates during the spontaneous imbibition measurements, then the wettability of the core can be determined from both the Amott wettability index and the spontaneous imbibition rates. This offers some advantages over the standard Amott test because it is based on additional data. The main problem with the Amott wettability test is that they are insensitive near neutral wettability. Furthermore, Amott test does not discriminate adequately between the systems that give high values of wettability index to water and are collectively described as very strongly water–wet (Anderson, 1987).

2.1.2 Qualitative Methods

Anderson (1986b) reviewed the advantages and limitations of all the qualitative methods-imbibition, microscope examination, flotation, glass slide, relative permeability curves, capillary pressure curves, capillarimetric method, displacement capillary pressure, permeability/saturation relationships, and reservoir logs. This section briefly reviews different qualitative methods, explained by Anderson (1986b), for the characterization of wettability.

2.1.2.1 Imbibition Method

This method is the most commonly used as it gives a quick and rough idea of the wettability. This method doesn't require any complicated equipments. In an imbibition test, a core at initial water saturation is first immersed in brine underneath a graduated cylinder and the rate and amount of oil displaced by brine imbibition are measured. The core is strongly water-wet if large volumes of brine are rapidly imbibed, while lower rates and smaller volumes imply a weaker water-wet core. If no water is imbibed, the core is either oil wet or neutrally wet. Non water-wet cores are then driven to residual oil saturation and submerged in oil. The imbibition apparatus is inverted, with the graduated cylinder below the core to measure the rate and volume of water displaced by oil imbibition. If the core imbibes the oil, it is oil-wet. The strength of oil-wetness is indicated by the rate and volume of oil imbibition. The core is neutrally wet If neither oil nor water is imbibed. Cores with fractional or mixed wettability will imbibe both oil and water.

2.1.2.2 Relative Permeability Method

Wettability controls the location, flow and spatial distribution of fluids in the core. Hence it is evident that wettability affects relative permeability. In this method, Craig's (1971) rules of thumb are used to distinguish between strongly water-wet and oil-wet systems based on characteristics of relative permeability curves.

1) Connate water saturations are usually greater than 20 to 25% PV in a water-wet rock, but less than 10% PV in an oil-wet rock.

2) Water saturation at which oil and water relative permeabilities are equal is generally greater than 50% in water-wet rocks and less than 50% for oil-wet ones.

3) The relative permeability to water at flood out is generally less than 30% in waterwet rocks, but from 50 to 100% in oil-wet ones.

Provided the relative permeabilities are based on the oil permeability at the connate water saturation as the base permeability.

2.1.2.3 Permeability/Saturation Relationships

In this method, the wettability is characterized based on connate water saturation and air permeability. A qualitative measure of wettability is obtained by plotting the connate water saturation vs. air permeability. If the core is oil-wet, the average connate water saturation is relatively low and the plot is nearly vertical extending over only a small saturation interval. For the water-wet case, the curve has a gentle slope and extends over a large saturation interval.

2.1.2.4 Microscope Examination

In this method, the wettability is determined from a description of the flow on a single pore level in an idealized porous medium during waterflooding. This description includes the structure of the residual oil and the changes in the location of the oil and water that occur during waterflooding. If the system is strongly water-wet, the water surrounds the grains as a thin film. The large pools of residual oil rest on a water film, while the smaller drops of residual oil form spherical drops in the center of the pores. If the system is oil-wet vice-versa will be the case i.e. the roles of the oil and water are reversed. If the system is intermediately wet, both oil and water will be found in contact with the rock surfaces and both can be found in the small pores.

2.1.2.5 Glass Slide Method

This method assumes that a glass surface is representative of the reservoir rock. In this method, a clean, dry glass microscope slide is suspended in a layer of crude oil floating on water in a transparent container, and then the slide is aged. The glass slide is then lowered into the water. If the slide is water-wet, the water quickly displaces the oil on the slide. On the contrary, if the slide is oil-wet, a stable oil-wet film is formed and the oil is very slowly displaced.

2.1.2.6 Floatation Methods

This method is fast and preferable only for strongly wetted systems. In this method, water, oil and sand are placed in a glass bottle. The bottle is shaken and the fate of sand grains is observed. If the system is strongly water-wet, clean sand grains will settle to the bottom of the bottle. Sand grains placed in oil will aggregate and form small clumps of grains surrounded by a thin layer of water. If the system is oil wet, some of the grains can be suspended at the oil/water interface. Oil-wet sand grains in the water will clump together, forming small oil globules coated with sand.

2.1.2.7 Capillary Pressure Curves

In this method, the areas under the capillary pressure curves are used to measure the wettability of the core. This is the basis of the quantitative USBM method discussed earlier.

2.1.2.8 Capillarimetric Method

In this method, the adhesion tension which is also called displacement energy is used to characterize the wettability of the core. If the core is water-wet, the displacement energy is positive, and the displacement energy is negative if the core is oil-wet.

2.1.2.9 Displacement Capillary Pressure

In this method, the wettability is characterized based on apparent contact angles calculated by using the displacement or threshold capillary pressure.

2.1.2.10 Reservoir Logs

There are two methods available to measure the wettability of reservoir rock with logs. The first method is based on the fact that the electrical resistivity of an oil-wet rock is higher than that of a water-wet rock at the same saturation. The formation is first injected with brine and then resistivity logs are run. Next, the formation is injected with the same brine which has a reverse wetting agent to change a water-wet formation to an oil-wet one. The logs are rerun to determine the reservoir wettability by comparing the two measurements. The second method involves comparison of logs with core data. The saturation of the formation measured with logs is converted into a capillary pressure curve. Then the wettability can be characterized by comparing this curve with a capillary pressure curve of a clean water-wet core.

2.2 Wettability Effect on Oil Recovery Efficiency

Morrow et al. (1986) reported that reservoir wettability has a direct influence on the recovery factors for the displacement of oil by water. But still determination of reservoir wettability and its effect on oil recovery are long-standing problems in reservoir engineering. Owens and Archers (1971) observed that waterflood oil recovery is greatest under strongly water-wet conditions. They predicted that as the water advancing contact angle increases there is steady decrease in oil recovery. Morrow et al. (1986) has also stated that wetting conditions other than strongly water-wet are frequently encountered and many actually are preferable.

Salathiel (1973) observed that oil recovery is highest in mixed wettability conditions. Salathiel (1973) explained this phenomenon by stating that strongly oil-wet paths through the rock are generated at those parts of the pore surface in contact with crude oil, while the remainder stays strongly water-wet. Salathiel (1973) concluded that these paths are connected in consolidated media and allow oil to continue to flow even at very low oil saturations. Laboratory-prepared, mixed-wettability systems gave low S_{or} by extended waterflooding.

Jadhunandan and Morrow (1991) investigated the relationship between wettability and oil recovery by waterflooding as well as the dominant variables that control wettability in COBR (Crude-Oil-Brine-Rock) systems using Berea sandstone. Yildiz and Morrow (1996) pushed forward this research and published their paper on the influence of brine composition on oil recovery which showed that changes in injection brine composition can improve recovery.

Since then Tang and Morrow (1998) progressed the research on the impact of brine salinity on oil recovery. Tang and Morrow studied the effect of brine composition on microscopic displacement efficiency of oil by waterflooding and spontaneous imbibition. They reported that with increase in cation valency for 1% solution of NaCl, $CaCl_2$ and $AlCl_3$, waterflood recovery increased and imbibition rate decreased. They further reported that, with the exception of $AlCl_3$, oil recovery generally increased (8 to 13% of the original oil in place "OOIP") with decrease in salinity. Furthermore, decrease in salinity of the injected brine resulted in wettability transition toward water-wetness. They also observed incremental oil recovered when the injection brine was switched, at high water cut, from high salinity brine to diluted brine.

Other researchers such as Webb et al. (2004, 2005) and McGuire et al. (2005) carried out an extensive research program on low salinity injection (LoSal™). These programs included numerous core floods at ambient and reservoir condition (temperature and pressure, with live fluid) both in secondary and tertiary mode, single well tracer tests and log inject log, which resulted in a series of publications and the registration of the LoSal™ EOR process trademark. Webb et al. (2005) showed a coreflood at reduced conditions (elevated temperature, reduced pressure, dead fluid system) and showed that there was no production benefit between the formation water (i.e. reservoir brine of 80,000 ppm TDS) and seawater floods. Figure 2.3 indicates that there was no benefit observed at the 30,000 ppm level; however, benefit was observed at the 1,000 ppm TDS level, i.e. there are no recovery benefits in injecting sea water even if the sea water salinity is less than the formation brine salinity.

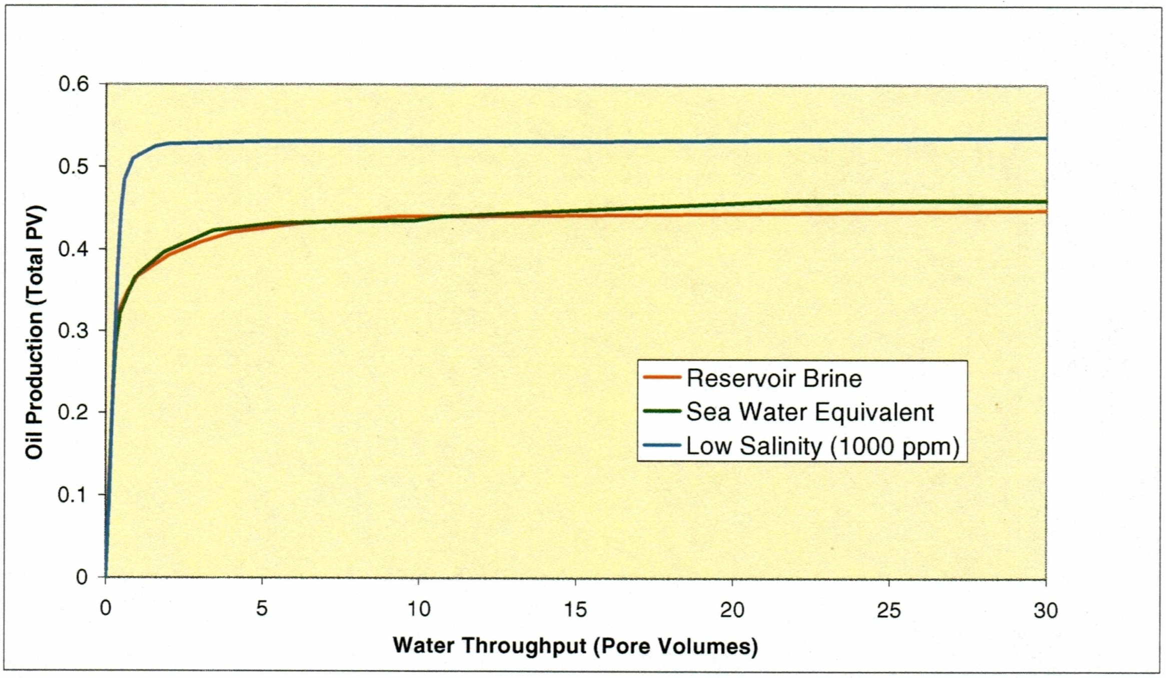

Figure 2.3 Comparison of High Salinity and Sea Water Waterflood Recovery at Reduced Conditions (Webb et al., 2005)

Agbalaka (2006) examined the impact of wettability alteration on reduction in the core residual oil saturation, S_{or} and the secondary oil recovery potential of low salinity brine injection at ambient and elevated temperatures using Department of Natural Resources (DNR) cores/Decane/NaCl brine system. In all experiments conducted Agbalaka (2006) observed a general trend that injection of low salinity water (2% and 1% NaCl salinities) result in higher volume of recovered oil compared to the high salinity waterfloods (4% NaCl salinity); additionally, increasing the temperature of the injected water results in increased recoveries for the high salinity and low salinity brines. For DNR core/ Decane/ NaCl system, the observed result indicated that the decrease in residual oil saturation corresponds to increase in water-wetness (see Figures 2.4, 2.5).

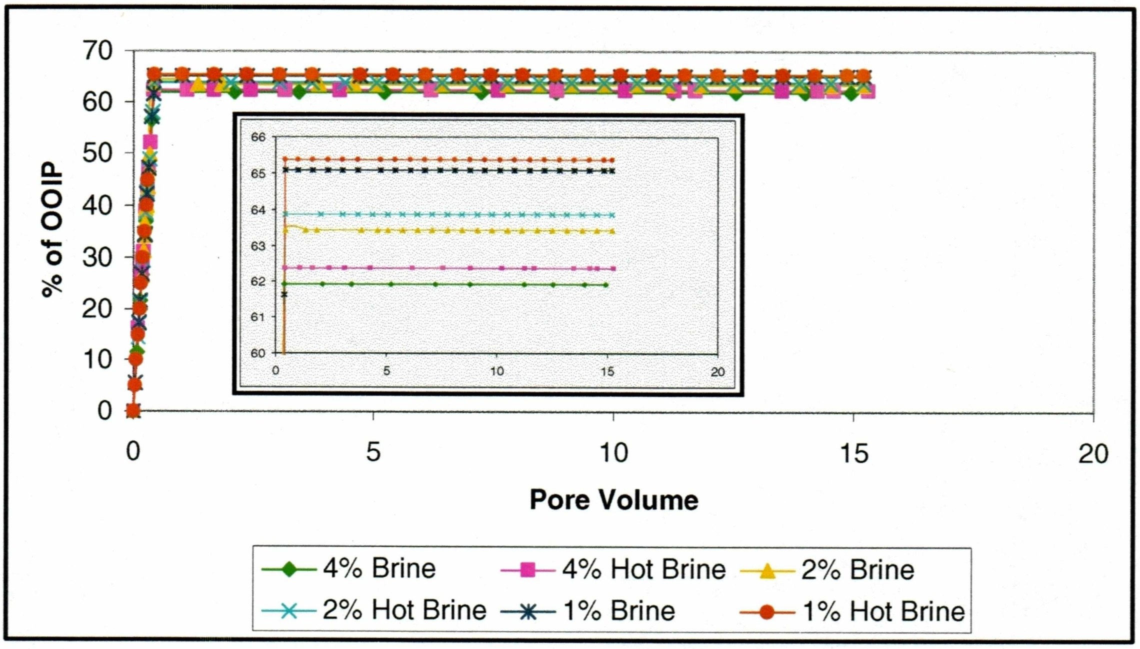

Figure 2.4 Oil Recovery Profile - Temperature & Salinity Effects, Core Sample #1 (DNR Cores / Decane System) (Agbalaka, 2006)

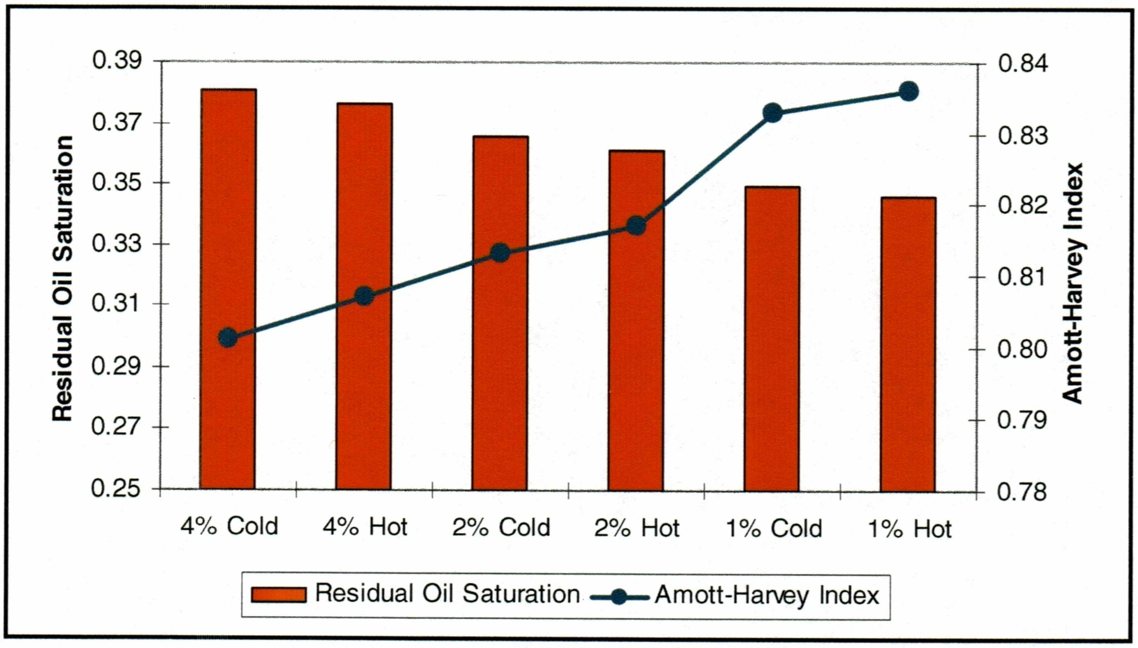

Figure 2.5 ROS - Temperature & Salinity Effects on Wettability, Core Sample #1 (DNR Cores / Decane System) (Agbalaka, 2006)

2.3 Speculated Mechanisms for Residual Oil Saturation Reduction in Low Salinity Waterflooding

Increase in recovery of crude oil with decrease in salinity has been observed for numerous laboratory waterfloods. Buckley et al. (1991, 1998) have shown that brine mediates adsorption from crude oil onto mineral surface. It has also been observed that brine properties such as pH, ionic species and salinity affect crude oil/brine/rock interaction and hence wettability. Consequently the properties of the connate brine and injection water brine should affect the rock wetting characteristics as well as oil recovery efficiency.

2.3.1 Fine Migration

Tang and Morrow (1998) tried to explain the mechanism as a result of which reduction in residual oil saturation is observed when low saline brine is injected. They noticed fines (mainly kaolinite) being eluted during low-salinity waterfloods on Berea core samples. They concluded that underlying surfaces gets exposed due to fines mobilization, which increased the water-wetness of the system. Clays remain undisturbed in the presence of high salinity brine, and retain their oil wet nature which results in poorer displacement efficiency. Tang and Morrow (1998) supposed that the detachment of mixed-wet clay particles from pores mobilized previously retained oil droplets attached to these clays, allowing an increase in oil recovery.

2.3.2 pH variation

Lager et al. (2006) in laboratory observed a rise in pH when waterflooding experiments were conducted with less saline brine. This rise in pH is due to two parallel reactions:

1) Carbonate dissolution and 2) Cation exchange.

Lager et al. (2006) explained that the dissolution of carbonate (i.e. calcite and/or dolomite) results in an excess of OH- and cation exchange occurs between clay minerals and the invading water. The dissolution reactions are relatively slow and dependent on the amount of carbonate material present in the rock

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO3^{2-} \quad \textbf{(2.5)}$$

$$CO3^{2-} + H_2O \longleftrightarrow HCO_3^- + OH^- \quad \textbf{(2.6)}$$

However, cation exchange occurring on the clay minerals, and to a much lesser extent quartz, is faster. The mineral surface will exchange H+ present in the liquid phase with cations previously adsorbed. This will lead to a decrease in H+ concentration inside the liquid phase resulting in a pH increase. If a pH above 9 was achieved inside a petroleum reservoir this would be equivalent to an alkaline waterflood. Here reduction of oil/water interfacial tension takes place at the front where alkaline water is displacing acidic crude oil. Hence higher oil recovery is observed during low salinity waterflooding.

2.4 Effect of Oil Aging on Wettability

Rock wettability has an important influence on multiphase fluid flow behavior in petroleum reservoirs. Although the adsorption of crude oil components by rock surfaces is believed to be one of the controlling factors of wettability, currently there is no satisfactory correlation that exists between crude oil composition and wetting tendency.

The types of mineral surfaces in a reservoir are also important in controlling wettability. Literature shows that carbonate reservoirs are typically more oil-wet than sandstone. Anderson (1986a) affirmed that when effects of brine chemistry are removed, silica tends to adsorb simple organic bases, whereas the carbonates tend to adsorb simple organic acids. This occurs because silica normally has a negatively charged, weakly acidic surface in water near neutral pH, while the carbonates have positively charged weakly basic surfaces. These surfaces will preferentially adsorb crude oil components/compounds of the opposite polarity (acidity) by an acid/base reaction. Wettability of silica will be more strongly affected by the organic bases, while the carbonates will be more strongly affected by the organic acids.

Generally it is believed that all reservoirs were initially occupied by water. Hence it is assumed that reservoirs were initially, especially sandstone reservoirs, strongly water-wet. With the migration of oil into the reservoir, the water is displaced firstly from the very large pores and then from progressively smaller pores until such a point where the capillary forces holding the water in the very small pores cannot be overcome by the displacing force of the oil. Over long geologic period surface active materials like polar compounds or high molecular paraffinic hydrocarbon from the oil, may deposit on the rock matrix, altering the wettability of the reservoir. Hence it is believed that the crude oil composition is important in wettability variation in the reservoir, a fact which has been demonstrated by several researchers. Besides the composition of the crude oil, the "ability of the oil to contact the reservoir rock surface" is equally as important in the wettability variation process.

Hirasaki (1991) observed that variations in wettability are often related to the presence or absence of stable water films between the oil and the reservoir rock surface. He reported that thickness of the water film determines the wetting in crude oil/brine/rock (COBR) systems. The system will behave as water-wet system if there exists a stable thick water films separating the oil from the rock. On the contrary, unstable films will rupture possibly leaving one to a few molecular layers of water, and the oil comes in close contact with the rock surface. Polar oil components can then adsorb or deposit on the rock surface. Asphaltenes have specifically been considered to be responsible for wettability alterations, due to their polar groups that may interact and bind to the mineral surface.

Suspected alteration of wettability during recovery of reservoir rock samples introduces uncertainty into the results of laboratory core analyses. During handling of cores, efforts were taken to restore native wetting conditions. Thus to achieve this condition i.e. to restore native wettability in the present experiments, the same set of cores were oil aged and then experiments were conducted on them. This way we are assuming that the oil aging process/technique would take the core samples to its original state of wettability, i.e. reservoir wettability.

CHAPTER 3

EXPERIMENTAL SET-UP

As stated earlier, the primary objective of this work was to experimentally evaluate, on the core scale, the effect on oil recovery through changes in brine salinity and core wettability in secondary oil recovery mode. Hence to conduct the coreflood experiments on the ANS cores, a coreflood rig was used. The coreflood rig was designed by previous researcher Agbalaka (2006) who worked on a similar study. All the coreflood experiments in this study were conducted in secondary recovery mode. In this chapter, overall description of the set-up/coreflood rig and the principle of operation of all the equipments used is discussed.

3.1 Outline of Coreflood Rig

Figure 3.1 shows the schematic of the coreflood rig with all the important components. An ISCO pump was used to pump the fluid (brine/crude oil) at either constant pressure or constant flow rate from accumulators (brine/crude oil) in to the core holder. Floating piston present in the accumulator separates the de-ionized water of ISCO pump and the fluid present in the accumulator i.e. core flood fluid. When injecting the brine, the oil accumulator valves are closed and when injecting oil, the brine accumulator valves are closed. The fluid pushed from the accumulators flows to the injection face of the core plugs in the core holder. The condition of overburden pressure is simulated by applying radial pressure on the inside rubber sleeve of the core holder which holds the core in place under an overburden pressure. During the core flooding experiments in order to measure the differential pressure across the core, the differential transducer DP-15 is used. For reservoir condition coreflood two additional equipments 1) Produced Fluid Separator (PFS) and 2) Back pressure regulator are incorporated in the set-up. PFS separates and measures the quantities of brine and crude oil coming out of the core holder. This data is recorded on computer through PFS interface box. (However, measurement of the quantities of brine and crude oil coming out of the core holder was done by visual observations, as PFS could not be used due to technical problems faced during its operation.) Back pressure regulator connected at the end of the set-up helps to built up the pressure (reservoir pressure) in the coreflood rig. Reservoir temperature is achieved by the use of thermal blankets capable of supplying heat within an inclusive temperature range of 75°F and 425°F.

A brief description of each of the equipments/tools used in the experiment is given in the section 3.1.1 through 3.1.9. Detailed description and principle, on which each equipment works, can be found in Agbalaka (2006).

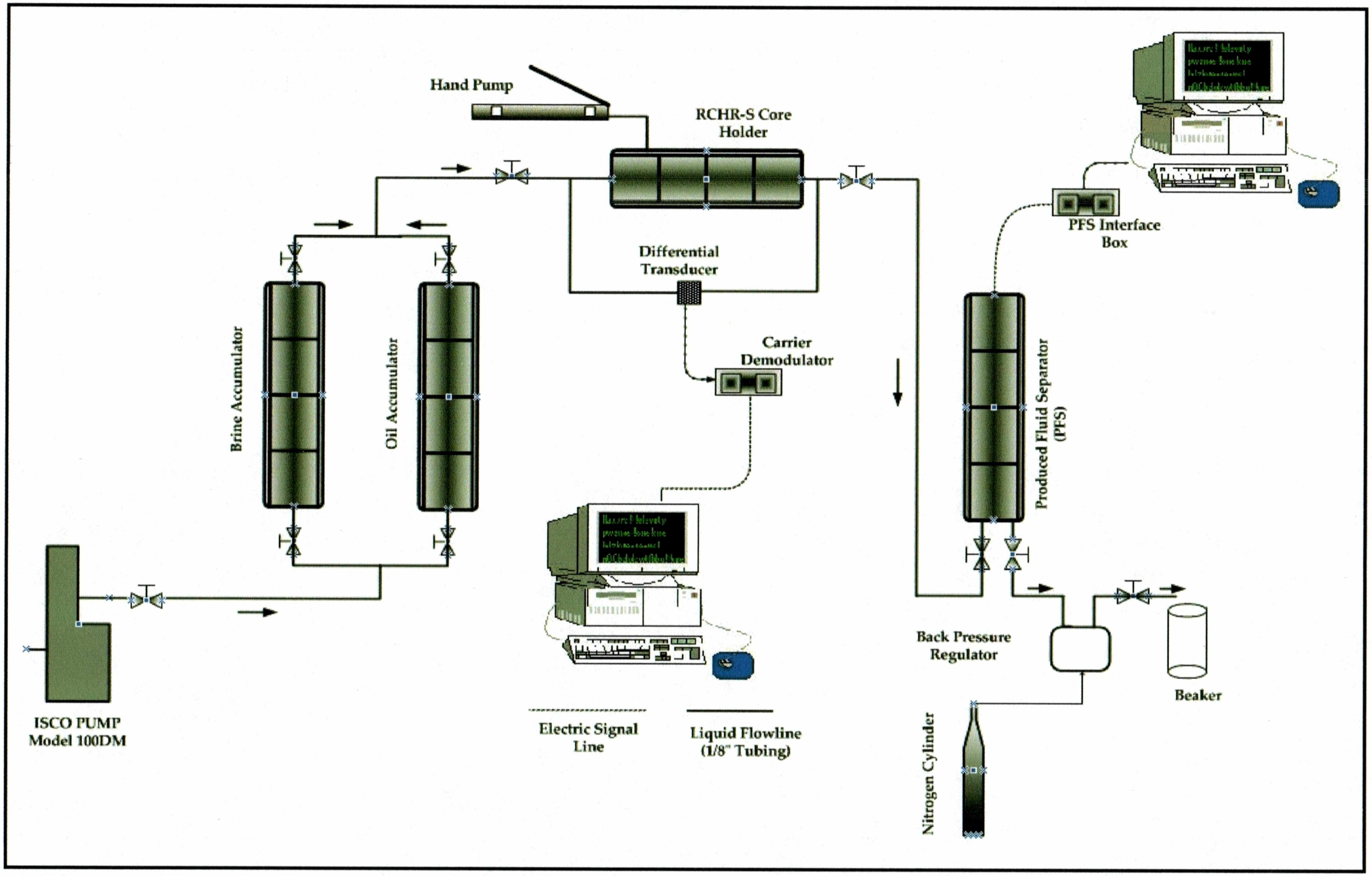

Figure 3.1 Diagrammatic Representation of Coreflooding Set-up (Modified after Agbalaka, 2006)

3.1.1 Fluid Circulation ISCO Pump

The Teledyne ISCO D-Series pump (model 100DM) was utilized for the circulation of fluid through the experimental system and for constant pressure maintenance through the entire system. The constant pressure mode maintains fluid delivery at a constant pressure by varying the flow rate. Whereas, for the constant flow mode, the flow rate remains constant by varying the pressure. Automatic and manual refill mode allows for the refilling of the pump cylinder with the displacing fluid (see Figure 3.2).

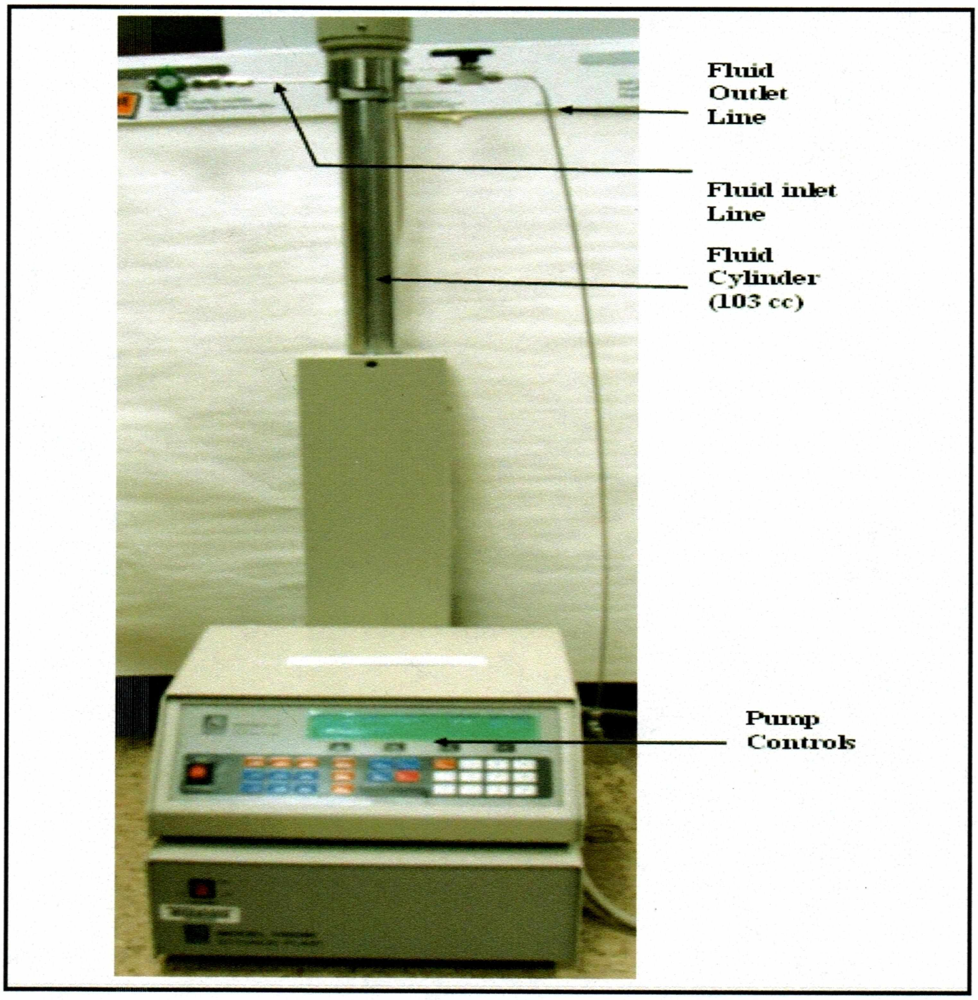

Figure 3.2 Teledyne ISCO D-Series Pump

3.1.2 Fluid Accumulators

An accumulator is a transfer vessel used for displacing fluids for core floods and similar displacement tests. For this work, two (oil accumulator and brine accumulator) (Model CFR-100-50) floating piston accumulators, manufactured by TEMCO were utilized. Both of them are rated at an operating pressure of 10,000 psi. Each of the accumulators has a capacity of 500ml and they can only be subjected to temperatures up to 350°F (see Figure 3.3).

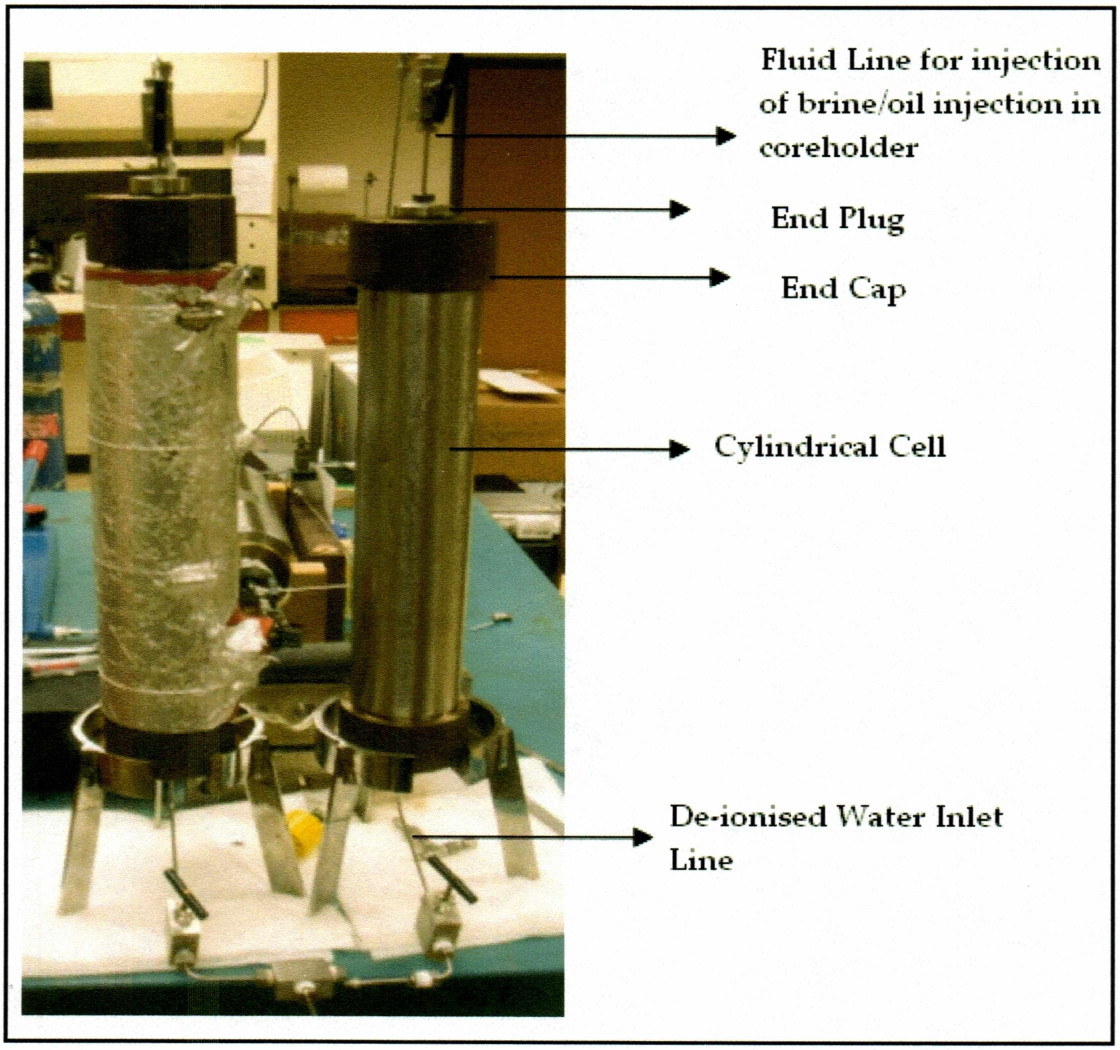

Figure 3.3 Fluid Accumulators

3.1.3 Core Holder

The core holder is used to confine the core plug in the core flood studies. The core holder used for this experiment is the TEMCO RCHR-series Hassler-type core holder. This Hassler core holder allows the application of overburden pressure in the radial direction. The core sample is held within the sleeve and the radial confining pressure simulates the overburden pressure. Two sizes of core plugs can be used with the TEMCO RCHR-series core holder: 1″ diameter and 1 ½″ diameter cores. The maximum useable core length is 6″. The core holder is rated at a maximum working pressure of 7500 psi and temperature of 350°F. Changing of the core plug is done by releasing the confining pressure, unscrewing the retainer, removing the distribution plug and taking out the core plug (see Figure 3.4).

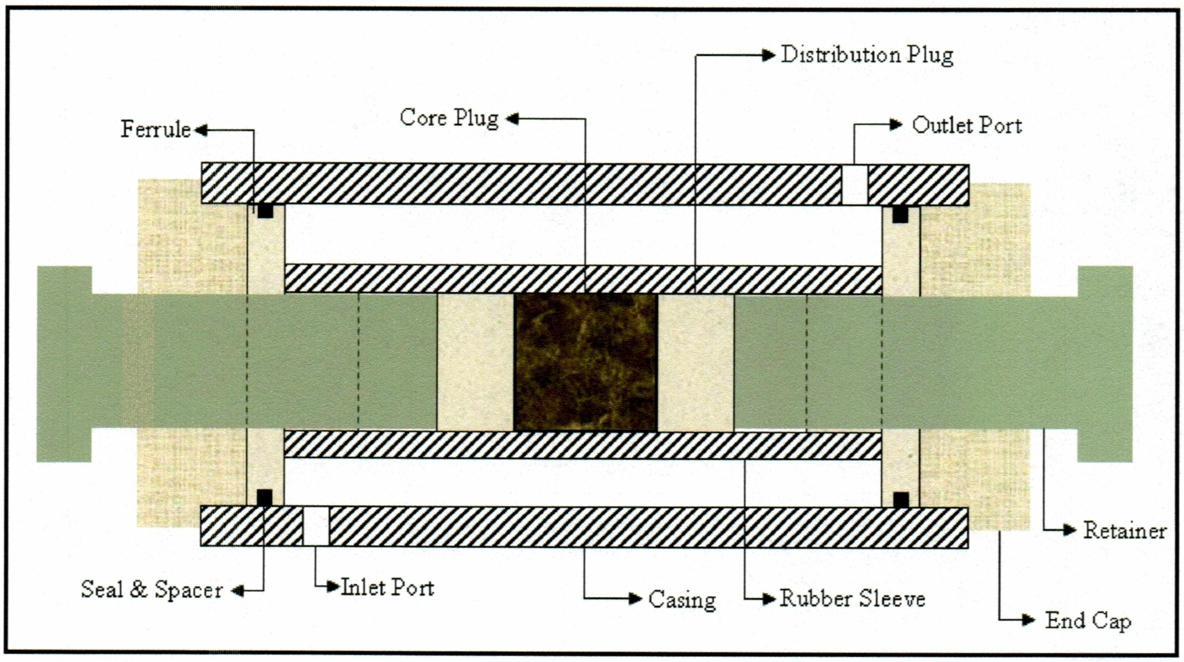

Figure 3.4 Schematic Representation of the RCHR-Series Hassler-Type Core

3.1.4 Hand Pump

The radial load necessary for simulating the reservoir overburden pressure was applied using the PH-Series (Model PH1) hand pump. The hand pump is operated by filling the fluids in the reservoir/chamber with required overburden fluid (typically hydraulic oil) and engaging the non-return valve (NRV). The pump outlet is connected to the bottom inlet port of the core holder. Through this inlet port, the hydraulic oil is pumped in the annulus of the core holder. When the annulus of the core holder is completely filled, the outlet port is sealed allowing a build up of pressure within the system up to the pre-determined value (see Figure 3.5).

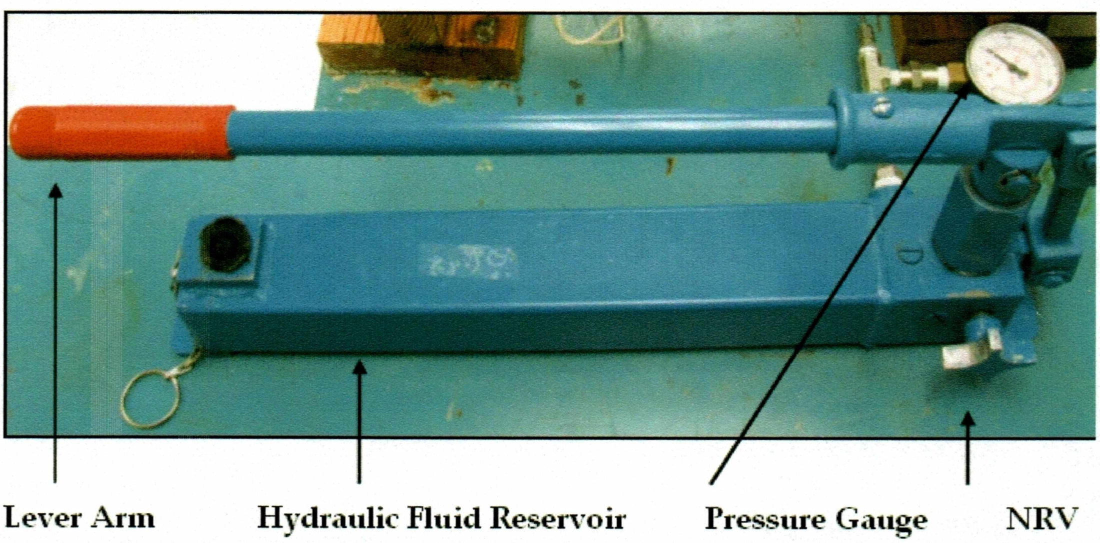

Figure 3.5 PH-Series (Model PH1) Hand Pump

3.1.5 Differential Pressure Transducer

Pressure drop across the core plugs was measured using the Model DP-360 differential pressure transducer manufactured by Validyne Engineering. The diaphragm present in the differential transducer undergoes elastic deformation when upstream and downstream pressures act on it. This results in proportional deformation of the diaphragm and it triggers a corresponding voltage change which is transmitted to carrier demodulator through an electrical cable present at the top of the differential transducer (see Figure 3.6).

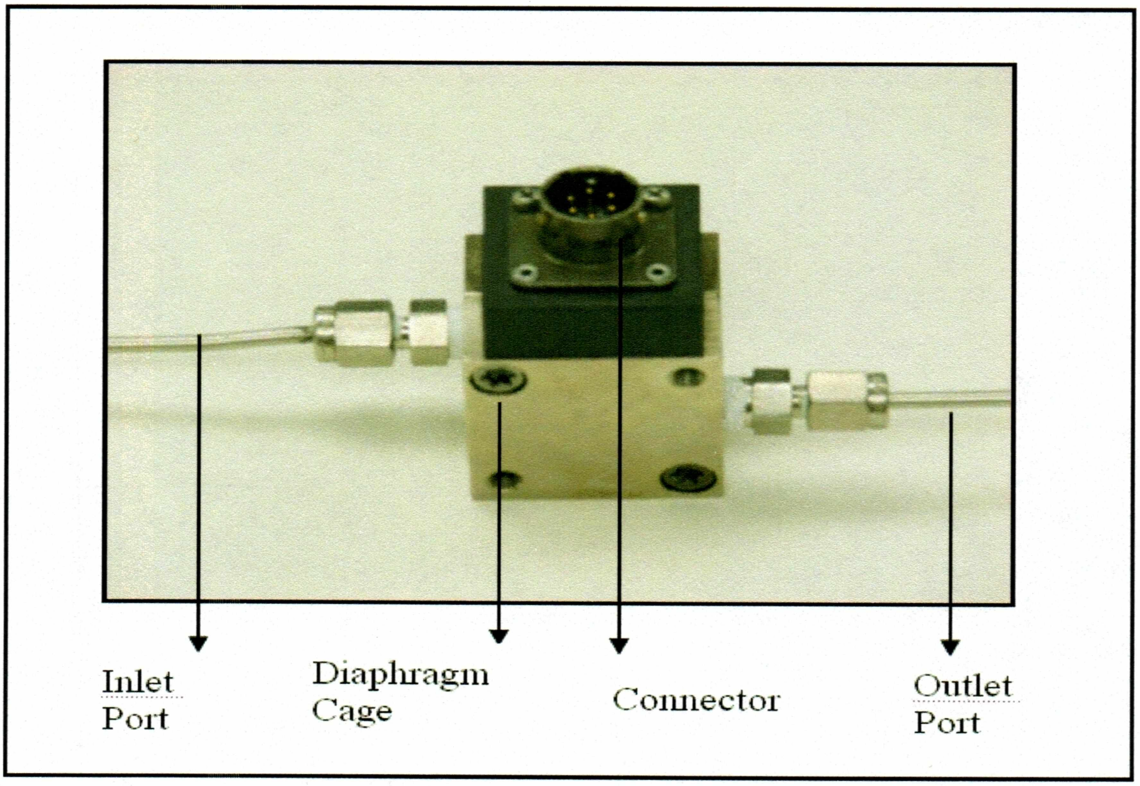

Figure 3.6 DP-360 Differential Pressure Transducer

3.1.6 CD-15 Carrier Demodulator

The sine-wave carrier demodulator converts voltage change signals obtained from the differential transducer into a computer readable signal. This demodulator is interfaced to a computer via a terminal block and cable to enable continuous data collection. To complete the interface, the MFC214 card, installed in the computer, is used as the voltage input A/D card. The MFC214 card accepts DC voltage inputs from the Validyne transducer. Data on the output pressure differential can be collected in its "raw" voltage form or scaled to record actual pressure data via the SC5 strip chart (see Figure 3.7).

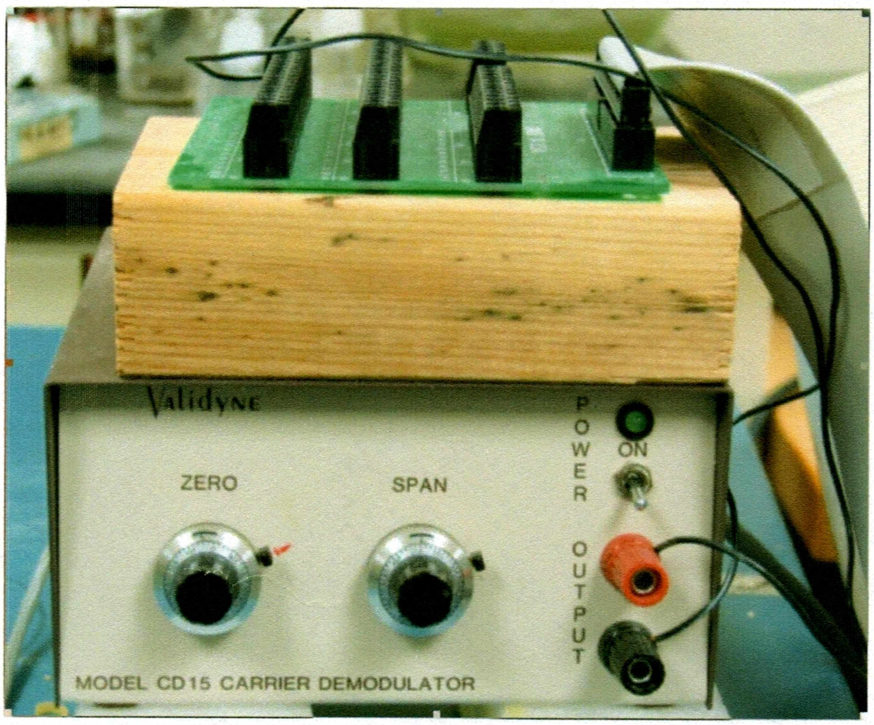

Figure 3.7 CD-15 Carrier Demodulator

3.1.7 Produced Fluid Separator (PFS)

As complete reservoir condition were not implemented in the coreflood experiments, PFS was not taken in to the operation. PFS is used to separate and measure the accumulation of produced oil and brine in waterflooding experiments. In a waterflood test, the effluent from the core is routed into the bottom INLET connection of the separator. The bottom exit port of the separator is used as the outlet from the separator and this port is either open to an ambient container or to a backpressure regulator. In the present study, to measure the accumulation of produced oil and brine is done by visual observation.

The PFS-092 (see Figure 3.8) measures the capacitance change of the non-conductive teflon tube as the conductive fluid moves along the tube length in contact with the conductive outer pressure vessel wall. As brine enters the tube, the capacitance increases. The change in capacitance changes primarily with the volume of the conductive fluid in the tube in a more or less linear manner. The computer queries the interface board which responds with a multi-digit hexadecimal return string. The computer decodes the string into the proper value and displays both the raw data value and the corrected value using the calibration factor.

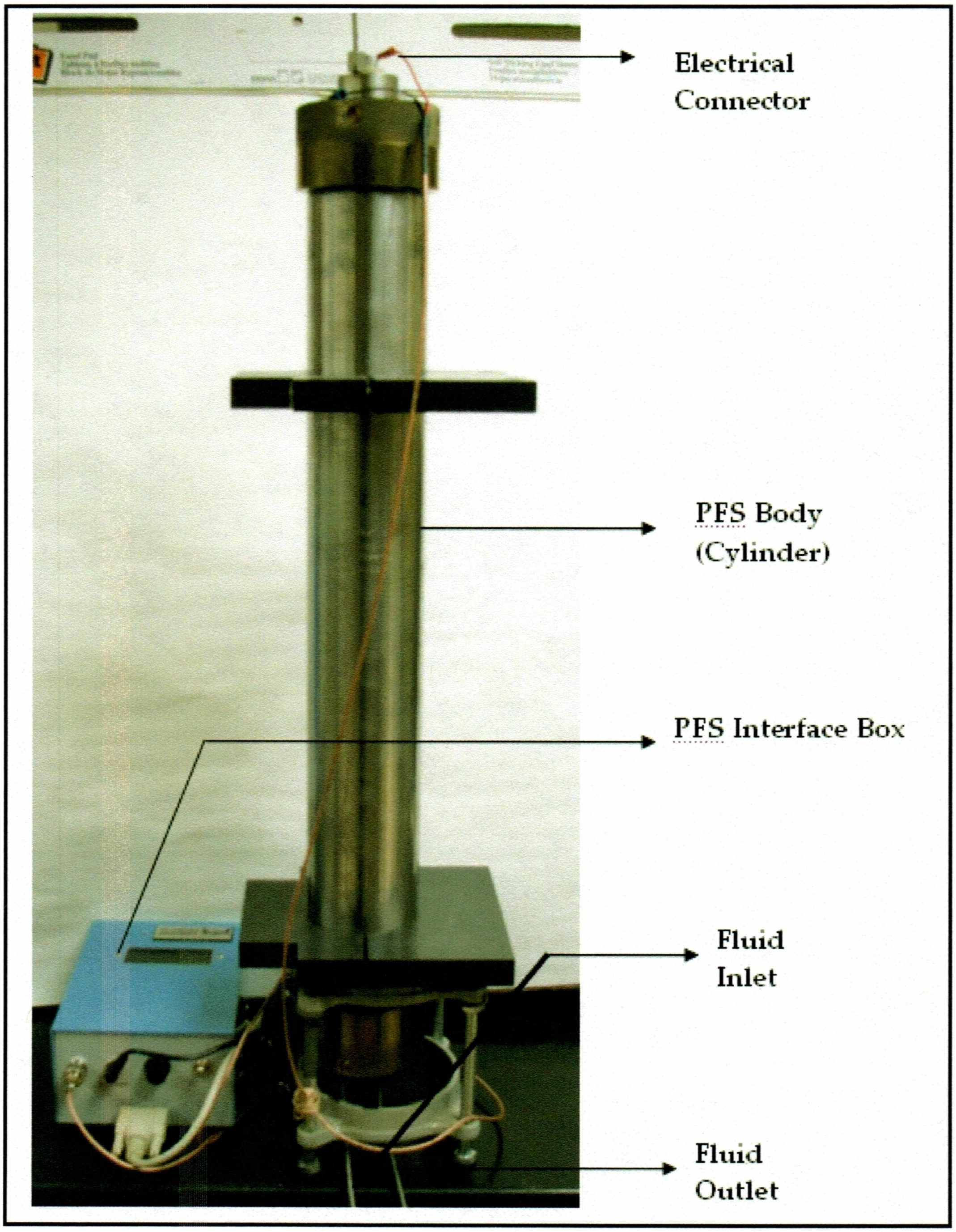

Figure 3.8 Produced Fluid Separator

3.1.8 Back Pressure Regulator

The application of the pressure regulator for this experiment is to maintain/simulate the actual reservoir pressure in the entire coreflood rig with a view to keeping the gas in solution when live crude oil is used. The back pressure regulator utilized has a maximum working pressure of 10,000 psi and temperature of 350°F (see Figure 3.9).

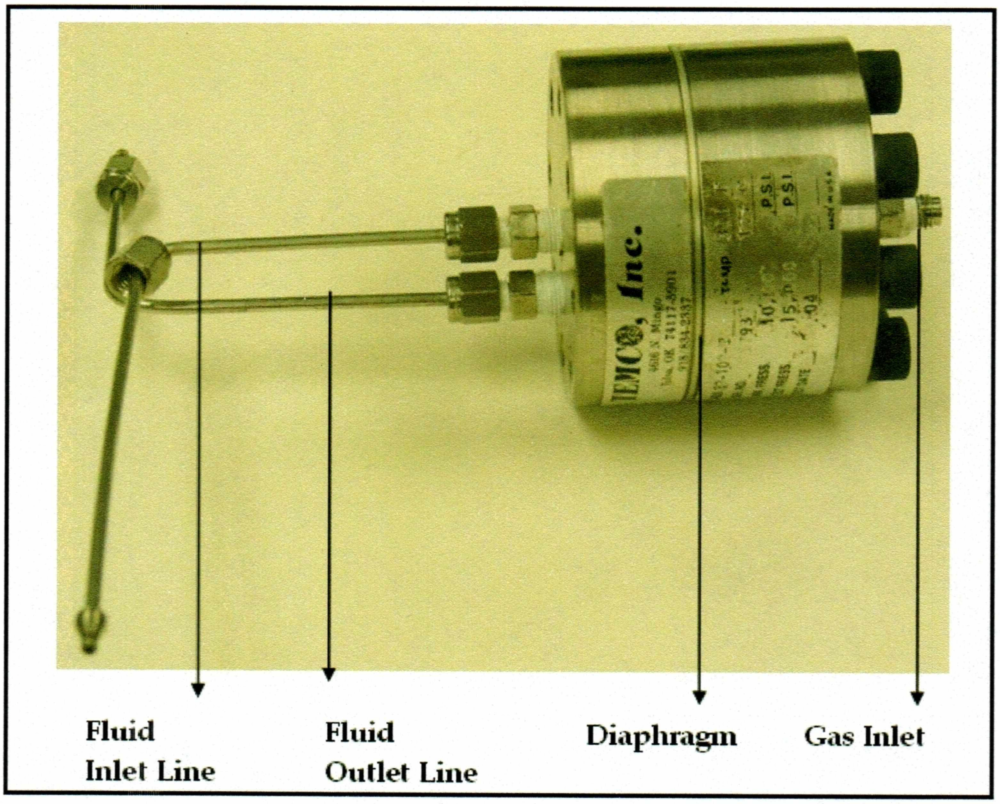

Figure 3.9 Back Pressure Regulator

3.1.9 Laminated Silicone Rubber Heater Blankets

Heating of the fluids, crude oil and brine, is achieved by the use of rectangular / square heater blankets. To prevent heat loss to the atmosphere from the heater blankets, the blankets are covered with materials having low heat conductivity. The experimental design allows for the use of four heater blankets for the following equipment: (1) oil accumulator; (2) brine accumulator; (3) core holder and (4) PFS.

3.1.10 Miscellaneous

Swagelok 1/8″ tubing was used to construct all the flow-lines of the coreflood rig. 1/8″ tubings were used in order to minimize dead volume and overall heat loss to the environment during hot water injection. For the gas supply to the back pressure regulator and for the calibration of the pressure transducer, pressurized nitrogen cylinders was used.

CHAPTER 4

EXPERIMENTAL PROCEDURE

The present research study was carried out on representative core samples from the Alaska North Slope. Three sets of experiments were carried out in this research study: 1) To observe the effect of variation in the brine salinity on the residual oil saturation and wettability of the new (clean) cores. 2) To study the effect of oil aging on the core samples and consequently observe the effect of variation in the brine salinity on the residual oil saturation and wettability of these oil aged cores. Reduction in salinity is achieved by reduction in the quantity of total dissolved solids (TDS) in the brine. Furthermore instead of reducing quantity of total dissolved solids (TDS) in the brine, the option of using the representative low salinity ANS lake water was also investigated. ANS lake water served the purpose of reduced salinity brine in the coreflood studies. Hence representative ANS lake water was also used in the experiments. Thus 3) the third set of coreflood experiments were conducted using ANS lake water to evaluate it's potential for secondary oil recovery and the associated wettability change, if any.

Flood rate for all the sets of experiments was kept at 30cc/hr. A reservoir temperature of 220°F was maintained. 500 psi overburden was used in the experiments. Wettability characterization for all set of experiments was done using the Amott-Harvey wettability index.

For the first two sets of experiments the brine was reconstituted in the lab while ANS lake water was used for the third set of experiments. The first step in all the experiments is the preparation of the core samples. The core plugs were prepared for use by pre flushing (with toluene, followed by acetone and then water) and/or heating. Subsequently porosities and absolute permeabilities of all the core samples were determined.

In all three sets of experiments, the core is then flooded to interstitial / initial water saturation and the initial wettability of the cores was determined using the Amott-Harvey test. The core sample is then waterflooded with brines of different salinity (at reservoir temperatures and ambient outlet pressure) and the waterflood oil recovery was noted. The wettability change, if any, is monitored at every stage of the experiment, (i.e. when the brine salinity is changed).

4.1 Core Samples

Ten representative ANS core samples were used for the present experimental research study. The cores were approximately 0.8″ in length and 1.5″ in diameter. Porosity and absolute permeability values were determined in the lab for all the core samples. Porosity values ranged from 19% to 32% while the permeability values were between 38 mD and 97 mD. Porosity was determined using the saturation method as described in section 4.4.2.1 of this work. Core permeability was calculated from Darcy's law based on the observed pressure drop across the brine saturated core after a steady state was achieved when injecting brine (22,000 TDS salinity) through the core sample.

Porosity and permeability values of all the ten core samples are shown in the following Figure 4.1.

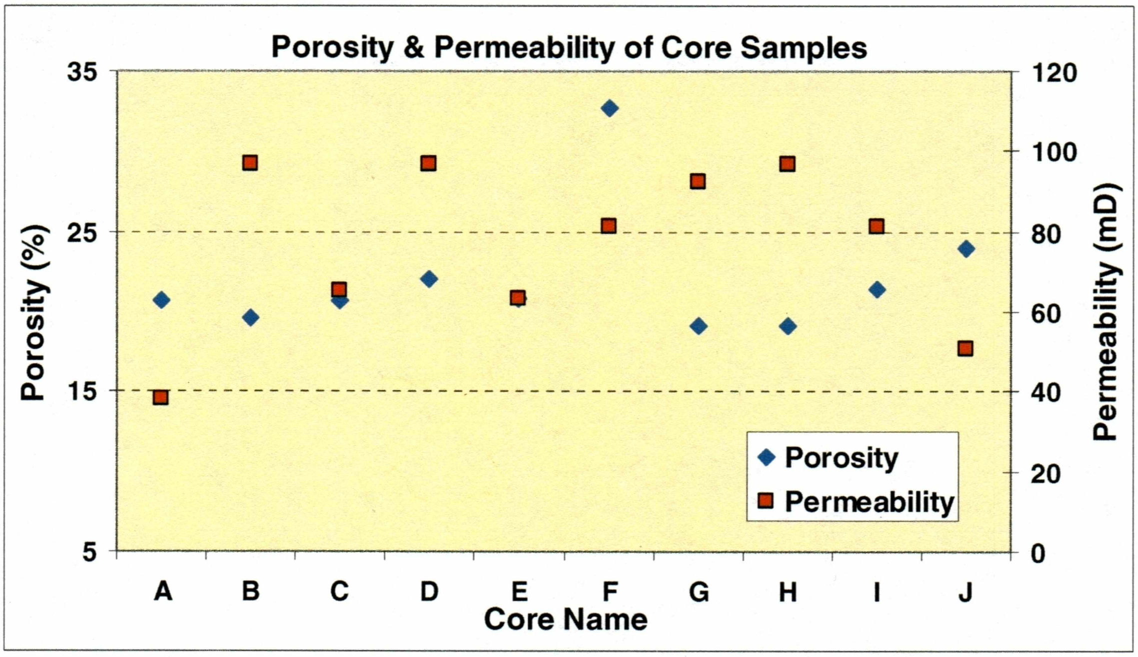

Figure 4.1 Porosity and Permeability Measurement of Tested Core Samples

4.2 Brine Sample

In order to simulate the representative ANS formation water composition of the reservoir, brine was reconstituted in the lab by dissolving different salts that included Sodium Bicarbonate ($NaHCO_3$), Sodium Sulphate (Na_2SO_4), Sodium Chloride (NaCl), Potassium Chloride (KCl), Calcium Chloride ($CaCl_2$), Strontium Chloride ($SrCl_2$), Magnesium Chloride ($MgCl_2$) in de-ionized water in proper proportion. Total dissolved solids (TDS) of the representative ANS formation water was based on the data reported by McGuire et al. (2005). Based on the composition (see Table 4.1), three different salinity brines viz. 22,000 TDS, 11,000 TDS and 5,500 TDS were prepared. For the first two sets of the coreflood experiments the lab reconstituted brine was used. While for the third set of experiments, actual ANS lake water and 22,000 TDS brines were used for coreflooding comparisons. The following procedure was followed to reconstitute the brine in lab:

1. Tare the balance scale with the empty measuring beaker on it
2. Fill the beaker with distilled/DI water and write down liters of distilled/DI water (L).
3. Based on the determined mass, calculate the mass (grams) of salt which when mixed with the distilled water gives 22,000 TDS salinity brine using the expressions given by equation 4.1.

$$\text{Required mass of each salt } (W) = (M * \text{Mol. Wt} * L * \varrho) / 10^6 \qquad \textbf{(4.1)}$$

Where M= Moles of salt

Mol. Wt= Molecular weight of salt

L= Liters of solution (brine) to be prepared

ϱ = Density of solution (brine) to be prepared.

The density of formation water at standard conditions can be estimated from the following correlation (McCain, 1991):

$$\text{Density} = 62.368 + 0.438603S + 0.00160074S^2 \qquad \textbf{(4.2)}$$

Where, S is the weight percent of total dissolved solids.

4. Weigh the calculated mass of salt; W, and mix with the distilled/DI water. Continue stirring until all the salt dissolves in the water.

The densities of different brines at ambient (77^0F) and reservoir temperature (220^0F) are tabulated in Table 4.2. Viscosity of the brine was measured using Brookfield Viscometer. At reservoir temperature viscosity observed was 1.10 cP.

Table 4.1 Composition of ANS Reservoir Water (McGuire et al., 2005)

Species (ppm)	Prudhoe Bay (PB) Aquifer
Barium	5
Bicarbonate	2060
Calcium	159
Chloride	11300
Iron	3
Magnesium	25
Potassium	78
Sodium	7860
Strontium	10
Sulphate	62
Total Dissolved Solids=	21,562

Table 4.2 Densities of Different Brines Used in the Experiment

Brine Salinity	22,000 TDS	11,000 TDS	5,500 TDS	ANS Lake Water
ϱ at 77^0F (g/cc)	1.0139	1.0065	1.0028	1.0002
ϱ at 220^0F (g/cc)	0.9590	0.9506	0.9471	0.9342

4.3 Crude Oil

Representative ANS crude oil (dead oil) was used for the present coreflood experiments. The density of the crude oil sample was measured using Anton-Paar Density Meter. The density was observed to be 0.8839 g/cc at the reservoir temperature (Approximately 220^{0}F).

4.4 Experimental Procedure

4.4.1 Core Cleaning

All the core samples for the experiment were cleaned before use. The cleaning process involved flushing the cores with toluene followed by acetone; the toluene was used to clean out/dissolve any hydrocarbon-based substance that may still be in the core while the acetone dissolved the toluene and/or water present in the core. Then the core plugs were dried in an air oven at 176^{o}F for at least 2 -3 days. After drying, the core samples were weighed to determine if they achieved a steady reading, indicating the removal of all native fluids.

4.4.2 Core Saturation

The dried core samples were weighed on a balance. The samples were then placed under vacuum for 5-7 days in 22,000 TDS salinity to allow equilibration time during which it is expected that the brine will achieve ionic equilibrium with the core sample.

4.4.2.1 Calculation of Pore Volume and Porosity

The porosity of the core plugs is calculated by the saturation method.

$$PV = \frac{M_{wet} - M_{dry}}{\rho_{brine}} \quad \textbf{(4.3)}$$

Where M_{dry} is the weight of the dry core, M_{wet} is the weight of the core after saturating with brine of known density, ρ_{brine}.

Porosity is then calculated as a percentage from the following expression

$$\phi = \frac{PV}{BV} \times 100 \quad \textbf{(4.4)}$$

4.4.3 Absolute Permeability Determination

Determination of the absolute permeability was carried out with the coreflood apparatus. A differential pressure transducer was connected to inlet and outlet ends of the core holder to measure the pressure drop across the core plug. Accurate determination of the absolute permeability depends on whether a steady-state condition is achieved within the core sample. Steady state condition is attained when the pressure drop across the core does not change with time. Figure 4.2 shows a typical plot of pressure drop vs. number of injected pore volumes (PV) of brine.

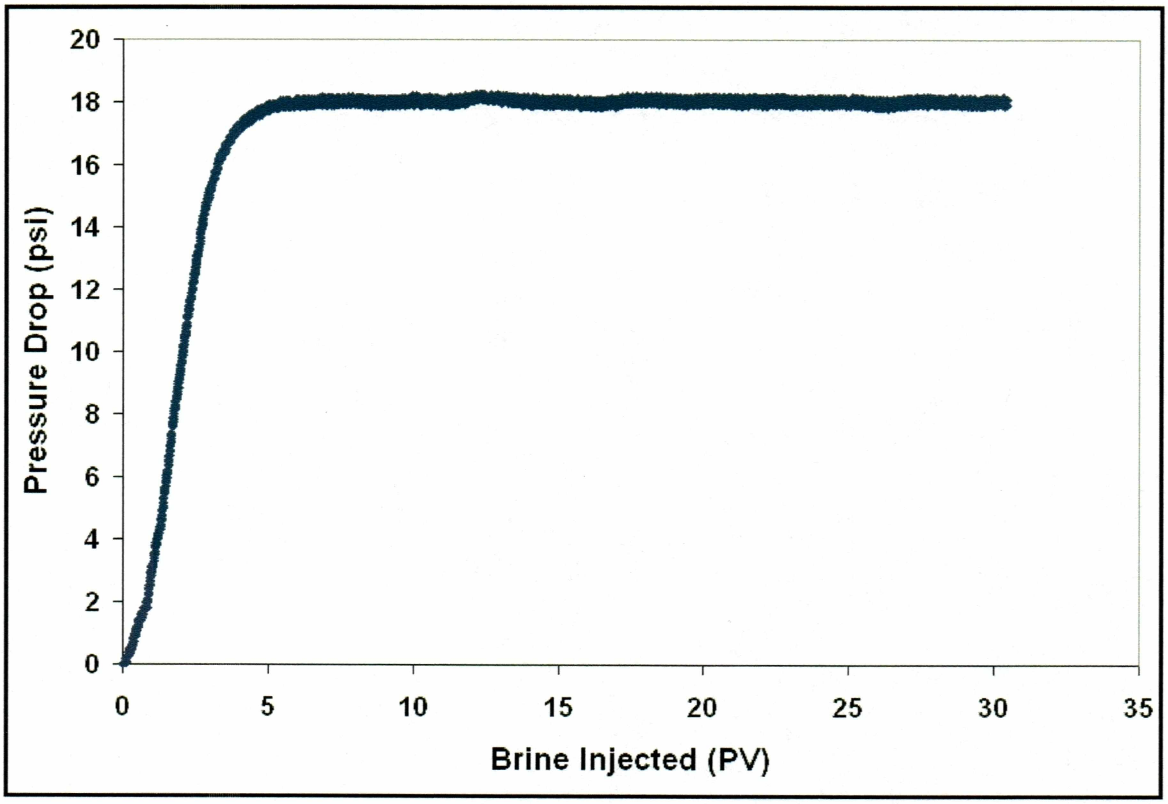

Figure 4.2 Pressure Drop Profile for Absolute Permeability Determination (Core E)

Calculation of absolute permeability (k) using Darcy Law:

$$k = \frac{[Q * dL * \mu]}{[A * dP]} \quad \textbf{(4.5)}$$

Where,

k = absolute permeability, Darcies

A = cross-sectional area, cm^2

dP = pressure differential, atm

dL = length, cm

q = flow rate, cm^3/sec

μ = viscosity, cp

4.4.4 Steps Followed in the First Set of Experiments

4.4.4.1 Initial Water Saturation Establishment

After calculating the absolute permeability of the clean core sample, the core is weighed and again confined in the Hassler core holder to flood it with crude oil in order to establish the initial water saturation. The rubber sleeve in the Hassler core holder helps in applying radial overburden pressure for the core sample. Hence an overburden pressure of 500 psi was applied radially on the core sample. Then the whole coreflood rig was raised to reservoir temperature with the help of heating jackets. The flooding was carried out at constant pressure drop of 300 psi. Displacement of water by oil continued until no more water was produced, which indicates the attainment of initial water saturation in the core sample.

4.4.4.2 Wettability Index (I_{AH}) Determination

Characterization/determination of wettability is achieved in this work by the modified Amott method (i.e. Amott-Harvey method) explained in section 2.1.1.3. The method consists of starting with the core sample at connate water-saturation. The core is then weighed and submerged in brine for 20 hours. During this 20 hours time period the brine spontaneously displaces oil. This spontaneously displaced volume (V_{osp}) was written down.

After the 20 hour immersion period, the next step was to weigh the core and insert into the Hassler core-holder for forced displacement of oil by brine.

The forced displacement was performed at a constant pressure drop at reservoir temperature. Injection of brine is continued until no-more oil is produced. The volume of oil forcefully displaced by brine, V_{ofd}, is measured in a metering cylinder. Thus the total oil volume displaced by water in spontaneous and forced displacement test is $V_{otot}= V_{osp}+V_{ofd}$.

The third step was to remove the core from the core holder and note its weight. Then the core sample was immersed in oil for 20 hours. The volume of brine spontaneously displaced by oil, V_{wsp}, is measured and the weight of the core taken after the 20 hour immersion period.

The fourth step was to load the core sample back in to the Hassler core holder and the brine is forcefully displaced by injecting oil at constant pressure. Oil injection is continued until no more water is produced. The volume of brine forcefully displaced, V_{wfd}, is noted and the mass of the core is taken after the forced displacement. Thus the total brine volume displaced by oil in spontaneous and forced displacement tests is $V_{wtot}= V_{wsp}+V_{wfd}$.

Then the Amott-Harvey wettability index is calculated by the following formula:

$$I_{AH} = I_w - I_o = (V_{osp} / V_{otot}) - (V_{wsp} / V_{wtot}) \qquad \textbf{(4.6)}$$

Amott-Harvey index (I_{AH}) varies from +1 for complete water wetness to –1 for complete oil wetness with zero representing neutral wettability.

4.4.4.3 Waterflooding

The next step in the present experiment was to carry out waterflooding on the core sample at reservoir temperature. After carrying out Amott-Harvey index measurement, the core was waterflooded by 22,000 TDS salinity brine and the recovery recorded as a function of time at a constant rate of 30cc/hr. After injecting 10 pore volumes (PVs) of 22,000 TDS brine, residual oil saturation (S_{or}) value was calculated. The wettability of the core plug is determined after this flood. This waterflooding procedure was repeated by using 11,000 TDS brine (reservoir temperature) and 5,500 TDS brine (reservoir temperature) and the respective S_{or} values were calculated. After every waterflood the Amott-Harvey wettability index was determined.

Using this procedure, the first set of experiment was carried out on 7 clean core samples. The results of these experiments are discussed in section 5.1.

4.4.5 Steps Followed in the Second Set of Experiments

The aim of the second set of experiments was to study the effect of oil aging on the core samples and consequently observe the effect of variation in the brine salinity on the residual oil saturation and wettability of these oil aged cores. Hence, after finishing the first set of experiments, the same core samples were used for second set of experiments. The first step in this set of experiments was to establish initial water saturation.

4.4.5.1 Oil Aging

After establishing initial water saturation, the core samples were removed from the core holder, immersed in steel tin containing ANS crude oil, and aged at 80°C to 90°C for 21 days. The tin was covered with a lid and aluminum foil to preclude the oxidation of oil during the aging period. After aging, cores were allowed to cool for a couple of hours.

4.4.5.2 Waterflooding

After oil aging for 21 days, the core samples were taken out from the tin and were brought for waterflooding experiments. In this set of experiments, the same reconstituted brines viz. 22,000 TDS, 11,000 TDS and 5,500 TDS were used. The steps followed in this case are the same steps followed in the new (clean) core samples. S_{or} values and the Amott-Harvey wettability index were calculated after every waterflood.

The results obtained for new (clean) and aged core are discussed in section 5.2 of the results and discussion chapter.

4.4.6 Steps Followed in the Third Set of Experiments

In the previous two experiments, the brine used for the corefloods was synthetically prepared/reconstituted brine in the laboratory. However, in this set of experiments the option of using the representative low salinity ANS lake water was investigated. Michael Lilly and Amanda Blackburn (Geo-Watersheds Scientific) helped to procure the ANS lake water. Based on personal communication with Amanda, it was learned that rain water and melting ice are the main contributors to water accumulation in ANS lake. So it is believed that the ANS lake water is much less saline. Total dissolved solids quantity in the water samples obtained from ANS was approximately 50-60 TDS. As ANS lake water is much less saline, the option of using ANS lake water as low saline brine was explored in the third set of experiments.

The steps followed in this set of experiments are the same as in the previous two cases. First, porosity and permeability of the core sample was determined. Then initial water saturation was established in the core sample followed by 22,000 TDS brine waterflood. However afterwards in the next steps of the experiments, instead of using 11,000 TDS and 5,500 TDS brine, ANS lake water was used for waterflooding. Thus ANS lake water serves the purpose of reduced salinity brine in these coreflood studies.

S_{or} values and the Amott-Harvey wettability index were calculated after every waterflood. The results of this set of experiments are discussed in section 5.3 of the results and discussion chapter.

CHAPTER 5

RESULTS AND DISCUSSION

In all the three sets of experiments the potential of the low salinity brine injection in secondary oil recovery was examined. For all three sets, an attempt was made to commence all the coreflood experiments at the similar initial condition i.e. the cores were at initial oil saturation (S_{oi}) and interstitial/connate water saturation (S_{wi}). An attempt is also made to explain any observed increase in recovered oil volume and reduction in residual oil saturation (S_{or}) in terms of change in wettability using the Amott-Harvey wettability index. The connate water salinity of the all the set of experiments was kept constant at a "high" salinity of 22,000 TDS, in order to mimic the reservoir saturation conditions.

In most of the experiments it is observed that there was an increase in oil recovery with a decrease in the salinity of the injected brine. Thus more oil is recovered when brine of a lower salinity is injected. It is encouraging to observe, in most of the experiments, a more or less consistent trend.

For the first sets of experiments, (i.e. on new (clean) cores), waterfloods were carried out using all the three brines viz. 22,000 TDS, 11,000 TDS and 5,500 TDS. After every waterflood the Amott-Harvey wettability index and residual oil saturation value were calculated. For the second set of experiments the cores used were the same cores on which previously the first set of experiments had been carried out. But before using these cores for the second set of experiments, these cores were oil aged for 21 days. Similar to the first set of experiments, waterfloods were carried out on these oil aged cores using all the three brines viz. 22,000 TDS, 11,000 TDS and 5,500 TDS. After every waterflood the Amott-Harvey wettability index and residual oil saturation value were calculated.

Results of Core E are considered here (see section 5.1, 5.2) as an example specimen for the discussion.

For the third set, experiments were carried out on new (clean) core samples. As stated earlier, waterfloodings were carried out using 22,000 TDS salinity brine and ANS lake water. Similar to the first two sets of experiments, after every waterflood the Amott-Harvey wettability index and residual oil saturation value were calculated. Results of Core H are considered here (see section 5.3) as an example specimen for the discussion.

5.1 Experiment on New (Clean) Cores

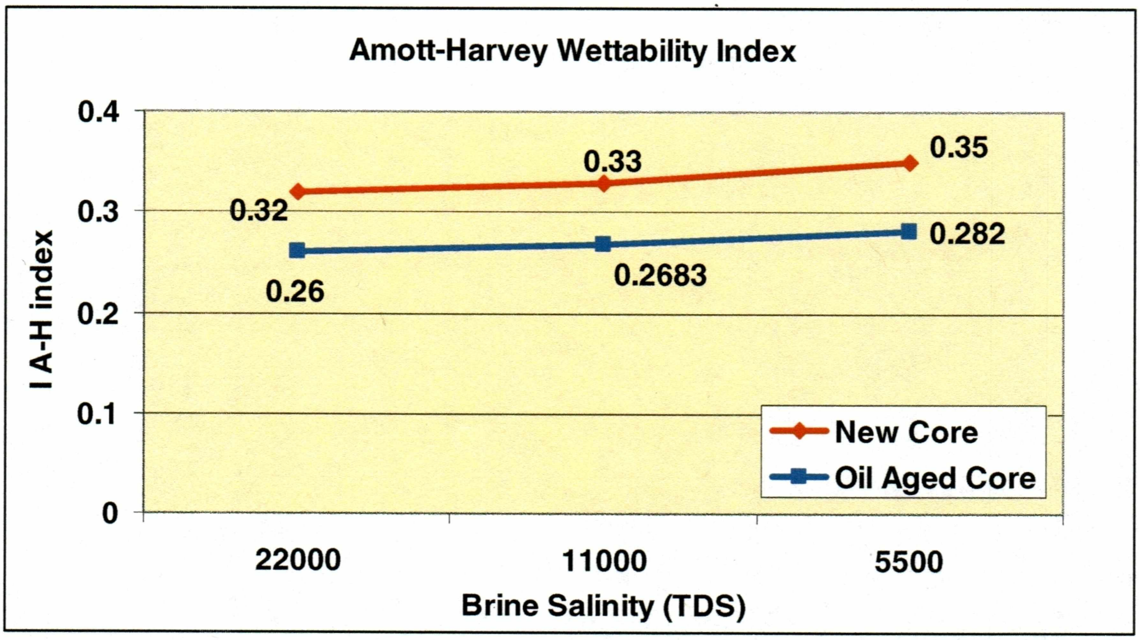

Figure 5.1 Effect of Brine Salinity on Wettability (Core E)

Figure 5.1 shows that when new (clean) Core E was waterflooded with 22,000 TDS brine the Amott-Harvey wettability index (I_{AH}) was observed to be

0.320. As the brine salinity decreased to 11,000 TDS, I_{AH} value increased to 0.330. Finally I_{AH} value increased to 0.350 when waterflooding was done with 5,500 TDS brine.

The Amott-Harvey wettability index (I_{AH}) is used to characterize the wettability of the cores. From Figure 5.1, it is observed that water wetness of the core increased slightly when it was flooded with less saline brine. However, the change in I_{AH} appears to be very marginal.

The residual oil saturation (S_{or}) value indicates how much oil is left behind in the pore space of the rock/core sample. When cores were flooded with different salinity brines, each waterflood resulted in a particular value of S_{or}. In case of the new (clean) Core E, when it was waterflooded with 22,000 TDS brine, it resulted in (S_{or}) value of 0.4077. But when brine salinity decreased from 22,000 TDS to 11,000 TDS to 5,500 TDS, the (S_{or}) value decreased from 0.4077 to 0.3837 to finally 0.3218, respectively (see Figure 5.2). It implies that when the core was flooded with 22,000 TDS brine the recovery was 36% of the original oil in place (OOIP). But when flooded with 11,000 TDS brine the recovery was 37% of OOIP and finally recovery rose to 50% of the OOIP when the core was waterflooded with 5,500 TDS brine.

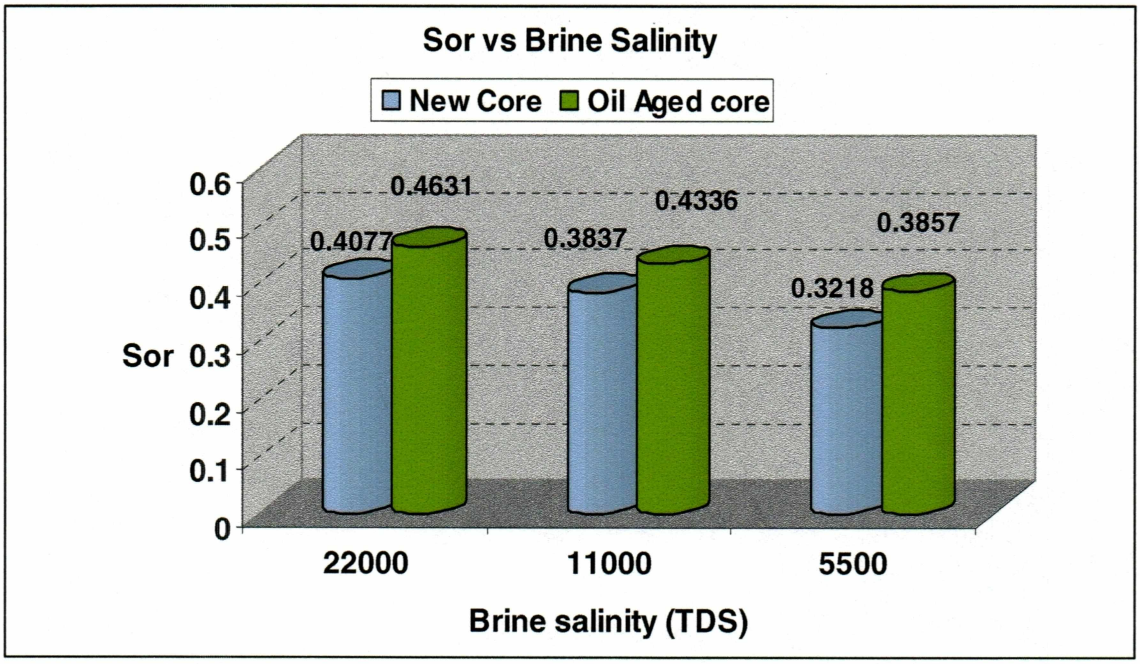

Figure 5.2 Effect of Brine Salinity on Residual Oil Saturation (Core E)

Thus, it is observed that there was an increase in oil recovery with a decrease in the salinity of the injected brine. Consequently, more pore volumes (PV) oil is recovered when brine of lower salinity is injected (see Figure 5.3).

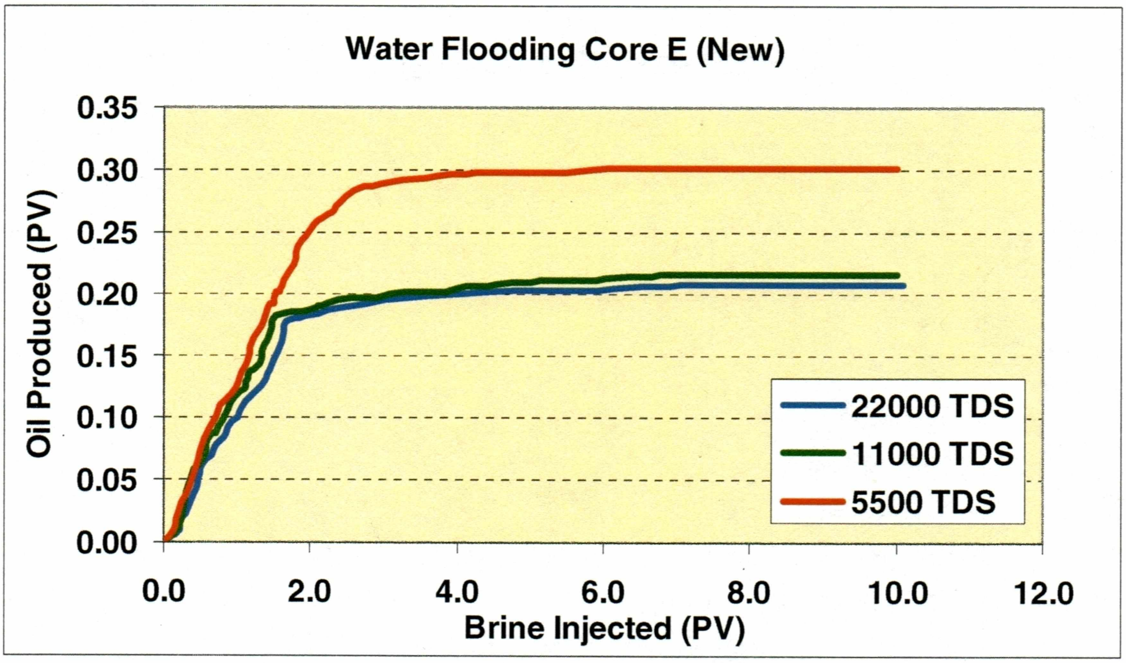

Figure 5.3 Oil Recovery Profile for New Core E

5.2 Experiment on Oil Aged Cores

When the same Core E was oil aged, Amott-Harvey index (I_{AH}) values decreased compared to its previous values when the core was new (clean). However, it's interesting to note that I_{AH} value increased from 0.260 to 0.268 to 0.282 when flooded with 22,000 TDS, 11,000 TDS and 5,500 TDS brine respectively. It shows that when the cores were flooded with less saline brine, it resulted in a slight increase in the water wetting state of the cores. However, this change in the I_{AH} appears to be marginal (see Figure 5.1).

It is also interesting to observe that when Core E was oil aged, there was an increase in the values of residual saturation compared to its residual saturation values when core was new (clean). However, it is also observed that as brine salinity decreased, the residual oil saturation value also decreased. When Core E was waterflooded with 22,000 TDS brine, it resulted in (S_{or}) value of

0.4631. But when brine salinity decreased from 22,000 TDS to 11,000 TDS to 5,500 TDS, the (S_{or}) value decreased from 0.4631 to 0.4336 to finally 0.3857 respectively (see Figure 5.2).

This implies that when core was flooded with 22,000 TDS brine the recovery was 31% of the OOIP. But when flooded with 11,000 TDS brine the recovery was 34% OOIP and finally recovery rose to 42% of the OOIP when the core was waterflooded with 5,500 TDS brine. As a consequence more pore volumes (PV) of oil are recovered when brine of lower salinity is injected (see Figure 5.4).

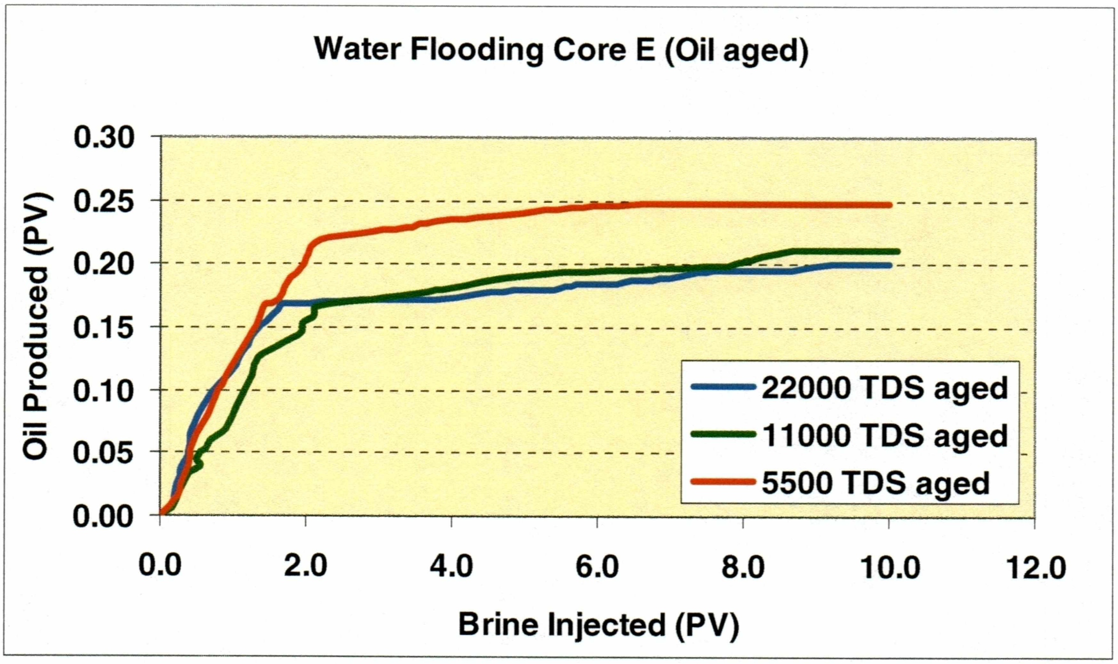

Figure 5.4 Oil Recovery Profile for Oil Aged Core E

Thus when waterflood experiments were conducted on oil aged core, it was observed that the wettability state of the core was shifted from a strongly water-wet (I_{AH} = +0.3 to +1.0) to a slightly water-wet (I_{AH} = +0.1 to +0.3) wetting state. The above stated observations for oil aged Core E can be attributed to the adsorption of polar compounds and/or the deposition of organic matter that was originally in the crude oil. As stated in section 2.4, surface active compounds in the crude oil are generally believed to be polar compounds that contain oxygen, nitrogen, and sulfur. These compounds are most prevalent in the heavier fractions of crude oil. It is believed that these compounds are responsible for altering the wetting state of the rock metrics/core surface.

Many researchers have proposed that the shifting of the wettability state towards a water wet state has given increase in oil recovery. Many have also proposed that shift towards oil wet state or intermediate wet state gives increased oil recovery. Consequently, it is believed that the observed incremental oil recovered and thus reduced S_{or} may be due to subtle alterations in wettability.

In the present study, for new (clean) and oil aged cores, the wettability of all the core samples is determined after each run using the Amott-Harvey wettability index. The measurements/characterization of wettability at every stage of run was done to validate the dependency of oil recovery efficiency on wettability and wettability variation.

As stated earlier, the general observed trend is a reduction in S_{or} and an increase in the Amott-Harvey wettability index with a decrease in the salinity of the injected brine at reservoir temperature. Plots show the variations in the values of the Amott-Harvey wettability index and the residual oil saturation with changes in brine salinity. From the graphs it can be understood that the shift towards a water wetting state resulted in a decrease of residual oil saturation.

Donaldson and Thomas (1971) reported that more oil is recovered from a water-wet system than from either the intermediate-wet or oil-wet system. While

Amott (1959), Rathmell et al. (1973), Morrow et al. (1986), Salathiel (1973) showed that that the alteration in wetting from strongly to weakly water-wet resulted in reduced S_{or}. Conversely, in the present study it is observed that as the Amott-Harvey wettability index increased i.e. water wetness increased, the residual oil saturation S_{or} value decreased. These observations are consistent with observations made in the literature by Tang and Morrow (1999), Sharma and Filoco (2000). The reason for this trend is not clear but as stated in section 2.3.1 Tang and Morrow (1999) supposed that the detachment of mixed-wet clay particles from pores mobilized previously retained oil droplets attached to these clays, allowing an increase in oil recovery.

5.3 Experiment Using ANS Lake Water

In the previous two experiments, the brine used for the corefloods was synthetically prepared/reconstituted brine in the laboratory. As the ANS lake water has much less salinity (approximately 50-60 TDS), in this set of coreflooding experiments the representative low salinity ANS lake water was used as an alternative to low saline brines viz. 11,000 TDS and 5,500 TDS brine. Results of specimen Core H will be discussed in this section.

Plots from these experiments show that incremental oil is recovered with a decrease in brine salinity of the displacing brine. Figure 5.5 shows that when new (clean) Core H was waterflooded with 22,000 TDS brine Amott-Harvey wettability index (I_{AH}) was observed to be 0.26. When the less saline ANS lake water was used, I_{AH} value increased to 0.29. However, the I_{AH} change appears to be marginal and takes place within the window of slightly water-wet characteristics when the core was flooded with less saline brine.

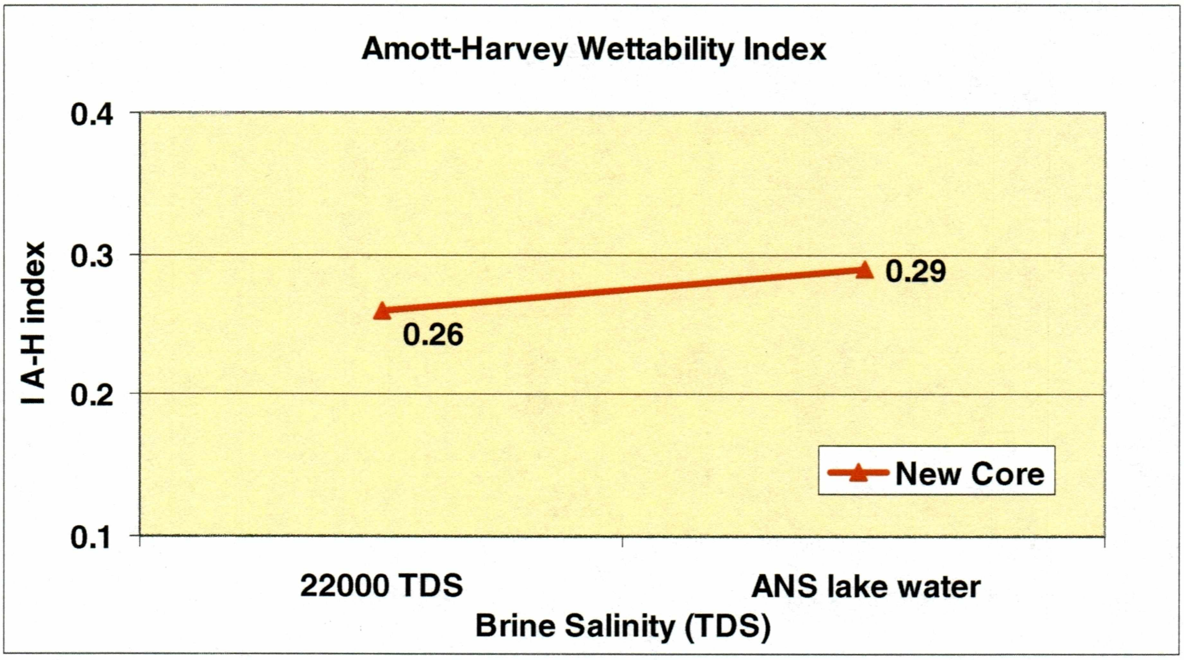

Figure 5.5 Effect of Brine Salinity on Wettability (Core H)

When the new (clean) core H, was waterflooded with 22,000 TDS brine, it resulted in (S_{or}) value of 0.3971. But when brine salinity decreased i.e. when the less saline ANS lake water was used, the (S_{or}) value decreased from 0.3971 to 0.2052 (see Figure 5.6).

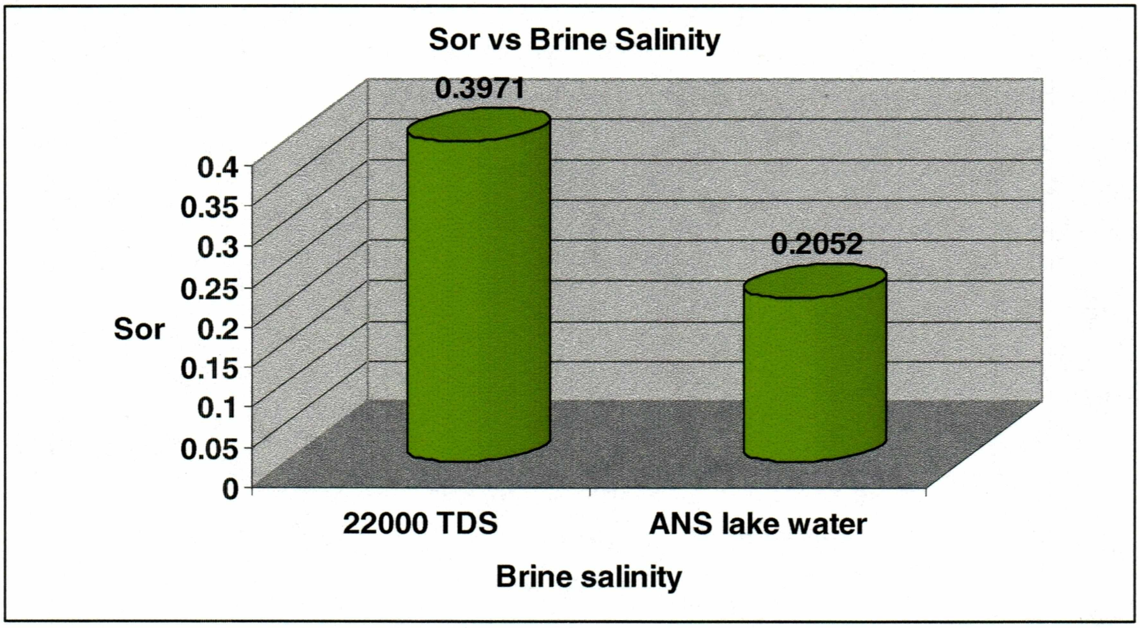

Figure 5.6 Effect of Brine Salinity on Residual Oil Saturation (Core H)

This means that when the core was flooded with 22,000 TDS brine the recovery was 40%. But when flooded with ANS lake water, the recovery was 68%. Thus more pore volumes (PV) of oil are recovered when brine of lower salinity is injected (see Figure 5.7).

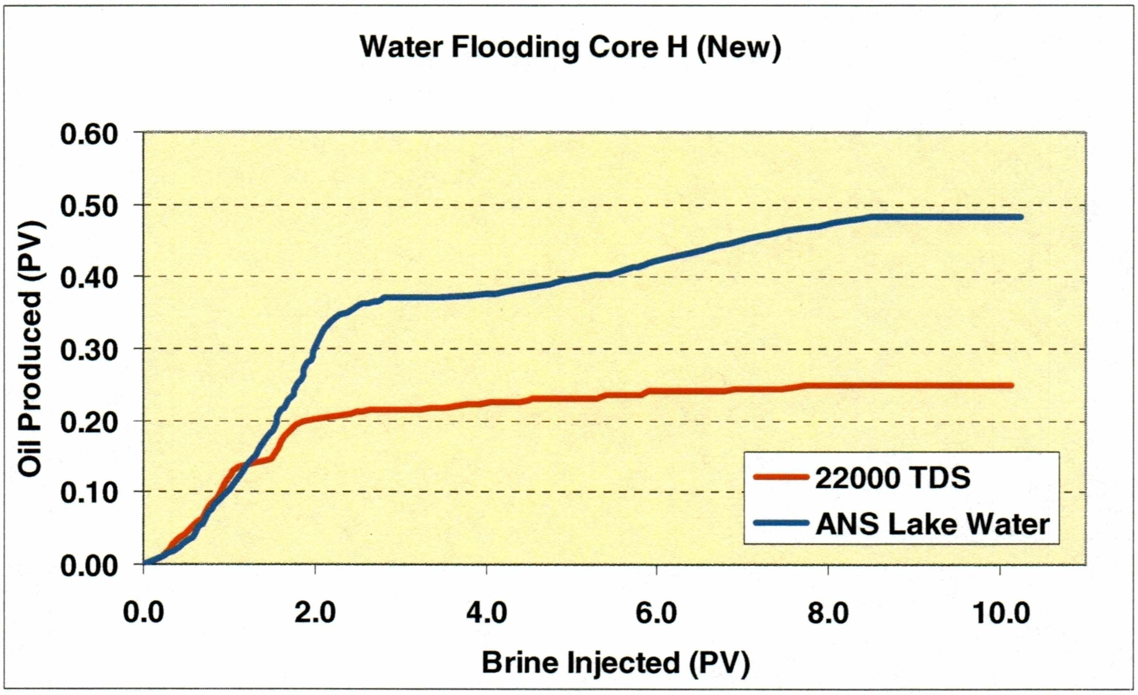

Figure 5.7 Oil Recovery Profile (Core H)

The first and second types of experiments were performed on seven ANS core samples. All of them have shown similar trends of results as like Core E (i.e. a slight increase in Amott-Harvey wettability index (I_{AH}) and a substantial decrease in residual oil saturation (S_{or}) as the salinity of the brine used for waterflooding is decreased). Whereas the third type of experiment was performed on three ANS core samples. It was interesting to observe that all of them showed similar trends of results like Core H (i.e. an increase in the Amott-Harvey wettability index and a decrease in residual oil saturation as the salinity of the brine used for waterflooding is decreased to that of ANS lake water).

The results obtained using ANS lake water are similar to some of the field or reservoir condition low salinity waterflood experiments done by other researchers. In laboratory tests of secondary recovery by injection of low salinity brine, Webb et al. (2005) reported that injection of 4,000 ppm brine into a reservoir core gave recoveries of up to 40% (~23% PV) higher than given by injection of 8,000 ppm brine. Whereas, in the present study that injection of ANS lake water (50-60 TDS) into ANS core gave recoveries of up to 68%, which is 28% higher than given by injection of 22,000 TDS brine.

McGuire et al. (2005) conducted the SWCTT (Single Well Chemical Tracer Tests) two in the Ivishak sandstone, one each in the Kuparuk and Kekiktuk sandstones. The results from the tests showed that waterflood residual oil saturation (S_{or}) were substantially reduced by low salinity water injection. The low salinity EOR (LoSal™) benefits ranged from 6 to 12% OOIP, resulting in an increase in waterflood recovery of 8 to 19%. Based on these encouraging results, low salinity oil recovery is being actively evaluated for North Slope reservoirs.

Formation water is one of the main sources for waterflooding process at ANS. Sometimes sea water is also considered for waterflooding process. Seawater salinity is typically 30,000-35,000 ppm, while formation waters can vary from almost fresh water to ~250,000 ppm, i.e. almost salt saturated (Webb et al., 2005). If the high saline water is diluted with less saline water then the resulting water would be of salinity which is higher than less saline water but would obviously be less than high salinity water. Thus in order to achieve low salinity water for waterflooding at ANS, diluting the formation water or sea water with less salinity water sources like ANS lake waters looks to be a promising option.

In Figure 5.8, results from different studies (McGuire et al., 2005; Webb et al., 2005; Agbalaka, 2006 and present study) are plotted to see how reduction in brine salinity results in a decrease of residual oil saturation or in other words how a decrease in brine salinity helps to increase the oil recovery. Figure 5.8 shows that as brine salinity decreased there is always a reduction in residual oil saturation, i.e. an increase in oil recovery. It is observed that when reduction in brine salinity is more than 80%, there is a significant increase in oil recovery.

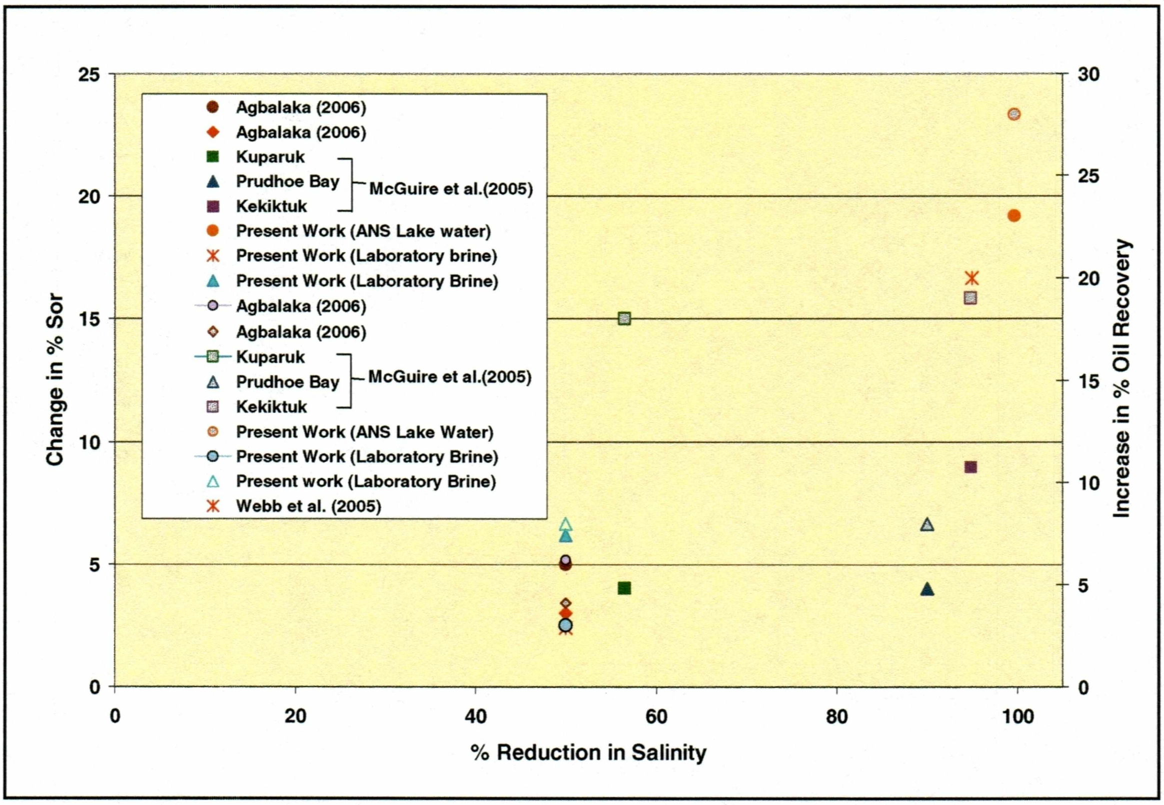

Figure 5.8 Increase in % Oil Recovery/Change in % S_{or} With Reduction of Brine Salinity for Different Studies

The results of the remaining core samples of the present study are shown graphically and summarized in a table in Appendix A.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1) The injection of low salinity brine at reservoir temperature, for the ANS crude oil/ANS new (clean) core system resulted in an increase in the Amott-Harvey wettability index and thus water-wetness of the core samples. This observed trend in wettability variation with reduction in brine salinity agreed with some of the published results of similar experimental studies.

2) The low salinity waterflood also resulted in an increase in the water wetting state of ANS crude oil/oil aged ANS core system.

3) The water wetness of the ANS core samples decreased when the cores were aged with ANS crude oil. Thus the Amott-Harvey wettability index (I_{AH}) shifted from strongly water wet to slightly water wet condition. However, the injection of low salinity brine resulted in a slight increase in the water wetness of the cores.

4) The low salinity waterflood resulted in a reduction in residual oil saturation (S_{or}) as the brine salinity decreased (from 22,000 TDS to 11,000 TDS and 5,500 TDS) for new (clean) as well as oil aged ANS core samples. Thus more pore volumes (PV) of oil are recovered when brine of lower salinity is injected.

5) Experiments performed using ANS lake water (50-60 TDS), which serves the purpose of less salinity brine, resulted in an increase of oil recovery. Hence, ANS lake water could be considered as a potential option of water

supply for the waterflooding process employed on North Slope. Alternatively, ANS lake water can be considered for dilution of the high salinity ANS reservoir brine.

6) Low salinity waterfloods have the potential for improved oil recovery in the secondary recovery process. This could be concluded on the basis of experimental results obtained from three sets of low salinity waterflood experiments, performed on Alaska North Slope core samples, carried out as part of the present study.

6.2 Recommendations

1) In order to evaluate the effect of solution gas in crude oil, corefloods need to be conducted at complete reservoir condition.

2) Imaging technology such as X-ray, CT scanning could be considered for detailed visualization of the pore space, especially at the residual oil saturation condition to determine the location of remaining oil. This will also help in better understanding of the relationship between wettability and residual oil saturation as much information can be obtained by visualization of the pore space.

3) Since low salinity ANS lake water floods showed promising results in terms of significantly reduced residual oil saturation, this water can be considered as a potential source for either direct injection or dilution of high salinity reservoir water to reap the benefits of low salinity waterfloods. However, a detailed study on the economics of these two options is worth considering for future work.

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APPENDIX

In Chapter 5, only the results of Core E and Core H were discussed. The results of the remaining eight core samples are listed here. For Core B, results of experiment conducted on new cores are only available as the core got damaged and hence experiments on oil aged Core B couldn't be conducted.

1) Core A

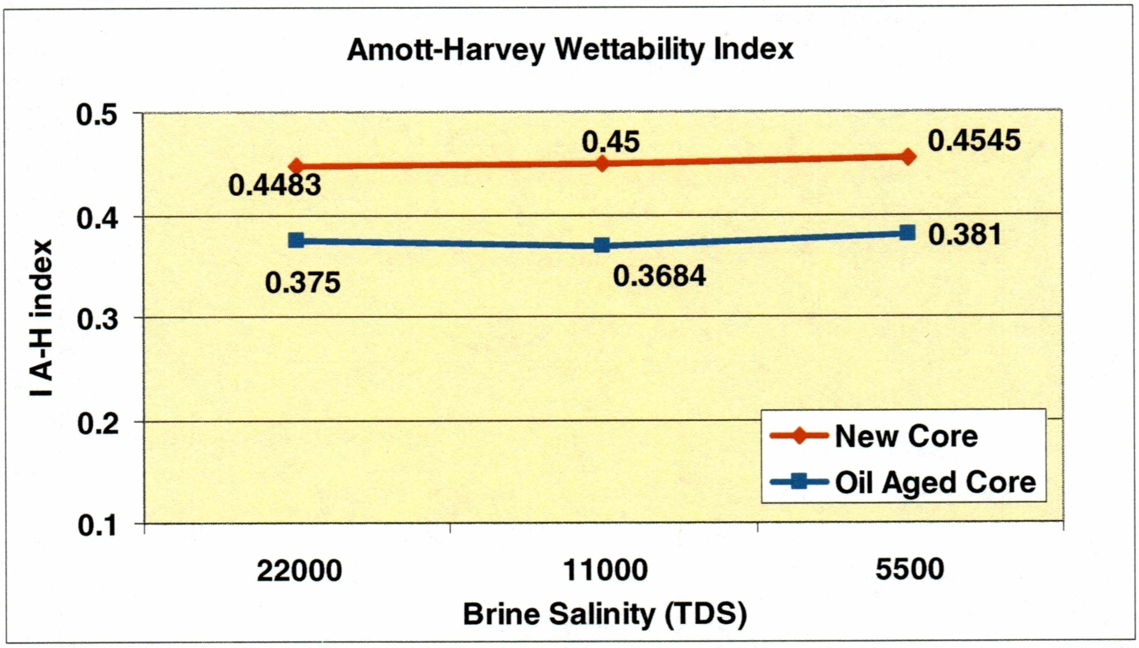

Figure A.1 Effect of Brine Salinity on Wettability (Core A)

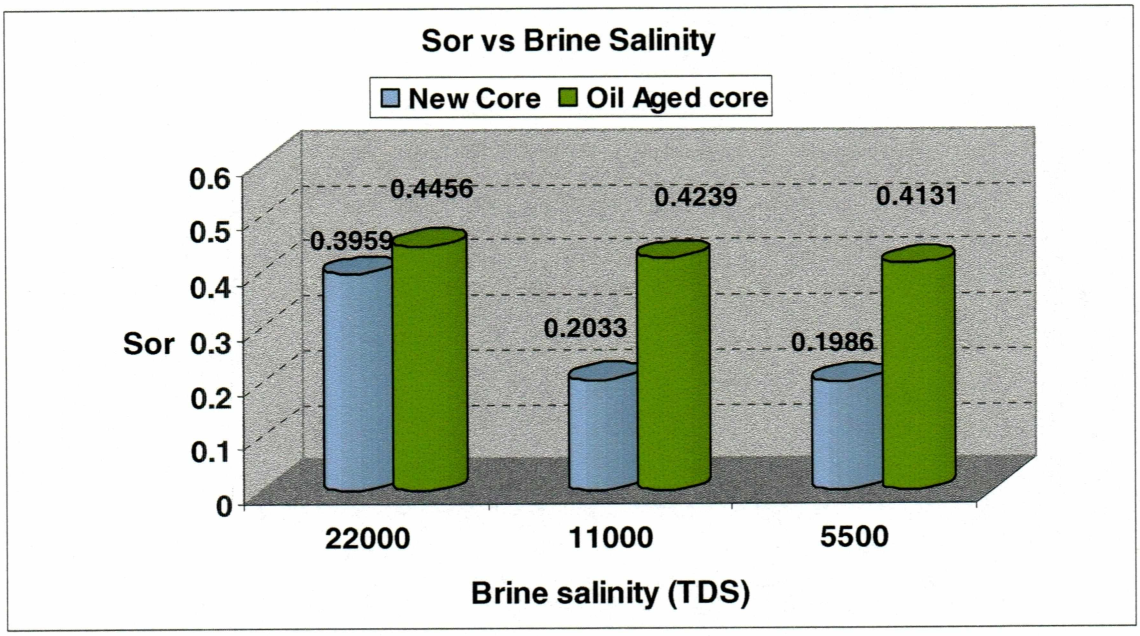

Figure A.2 Effect of Brine Salinity on Residual Oil Saturation (Core A)

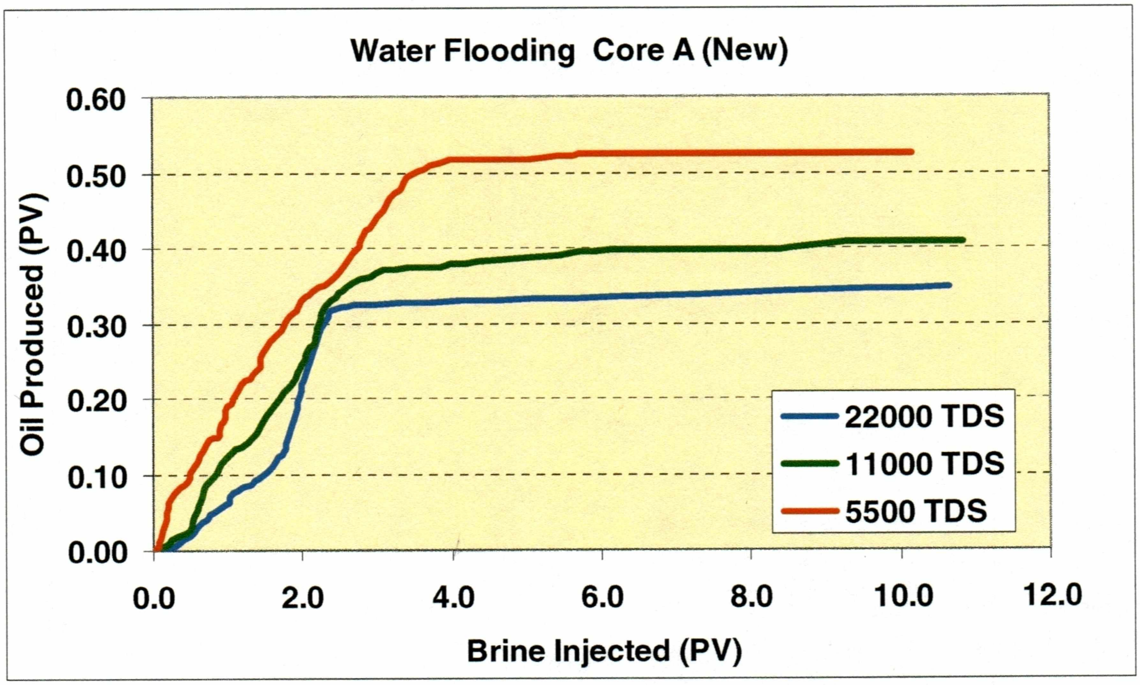

Figure A.3 Oil Recovery Profile for New Core A

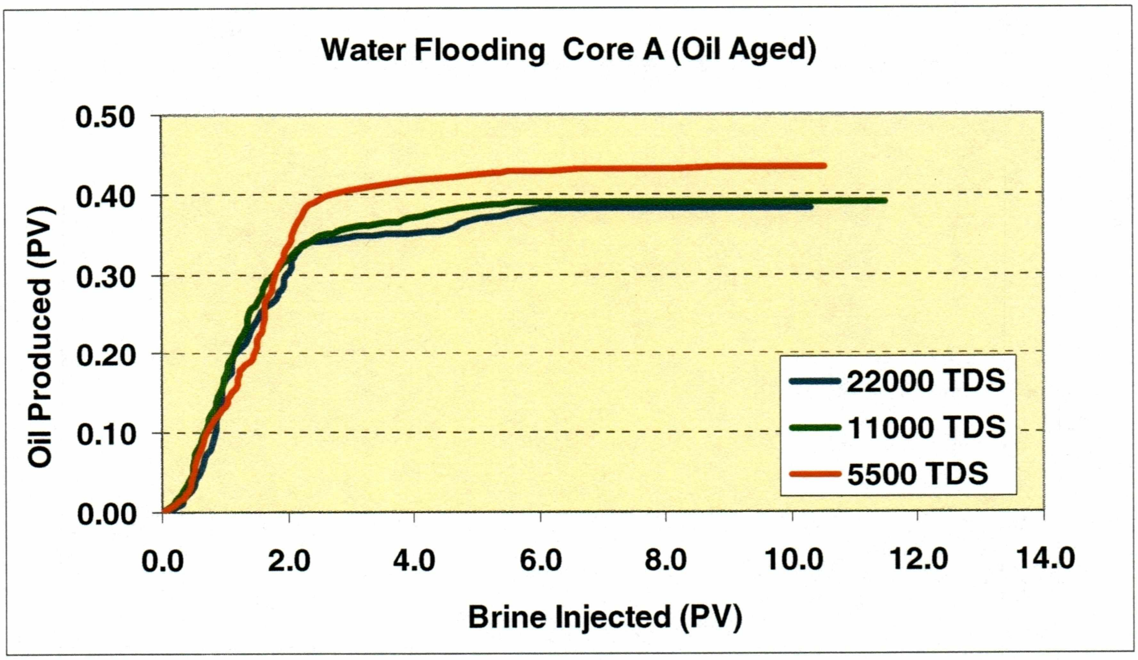

Figure A.4 Oil Recovery Profile for Oil Aged Core A

2) Core B

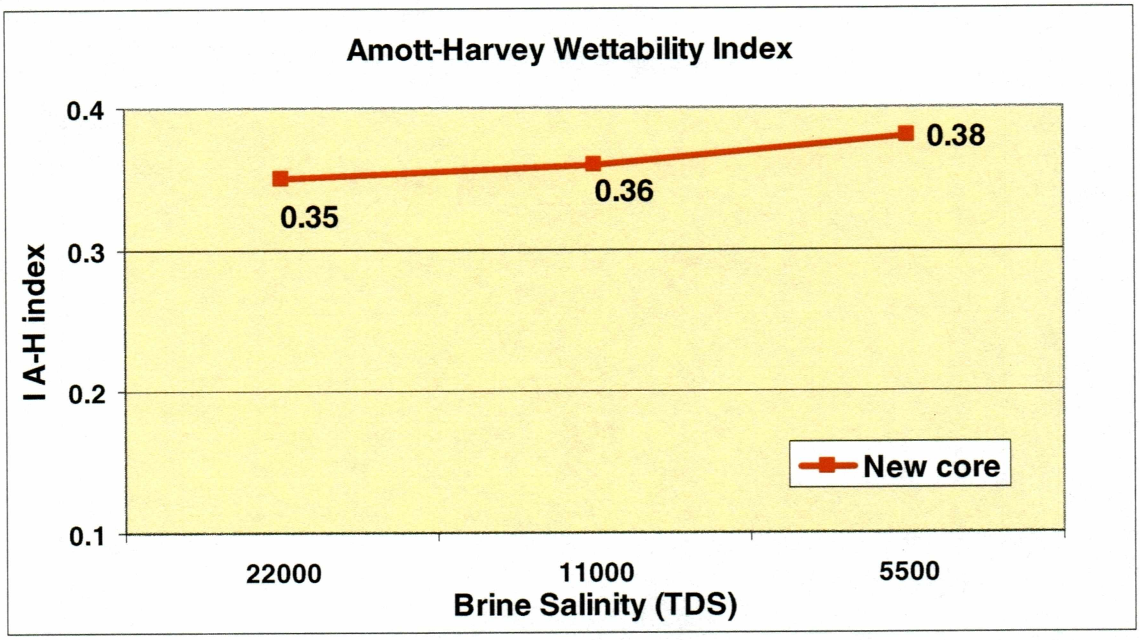

Figure A.5 Effect of Brine Salinity on Wettability for New Core B

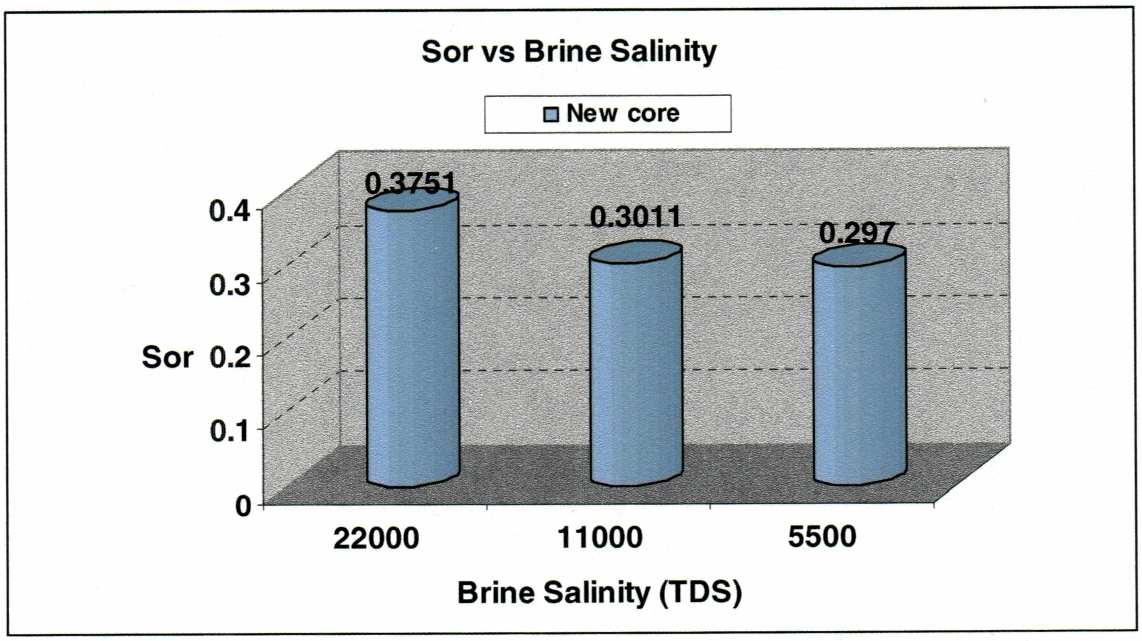

Figure A.6 Effect of Brine Salinity on Residual Oil Saturation for New Core B

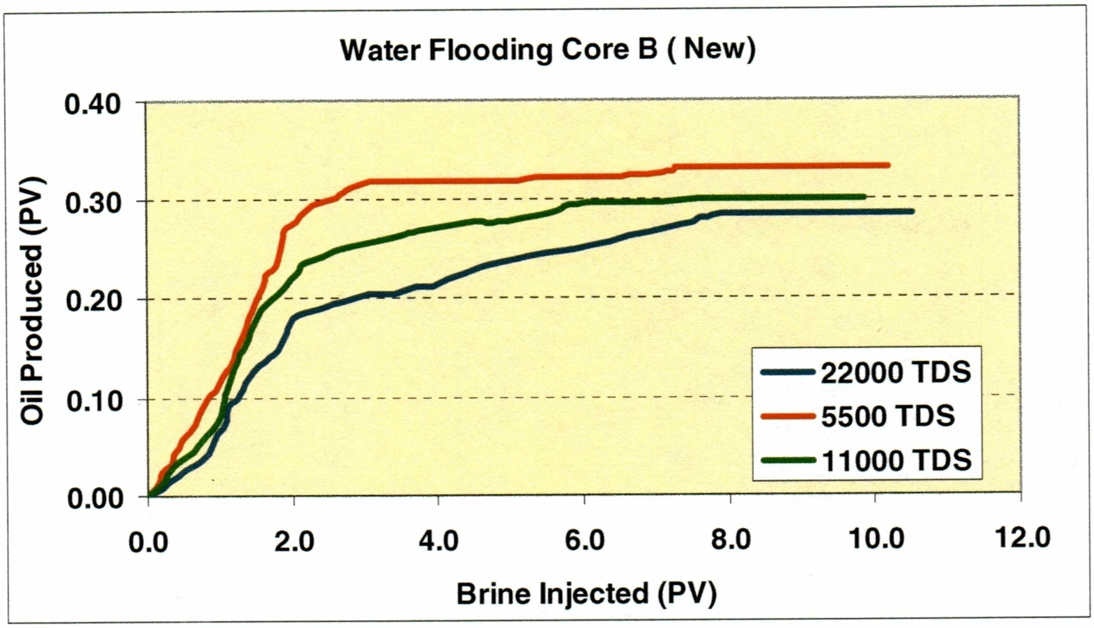

Figure A.7 Oil Recovery Profile for New Core B

3) Core C

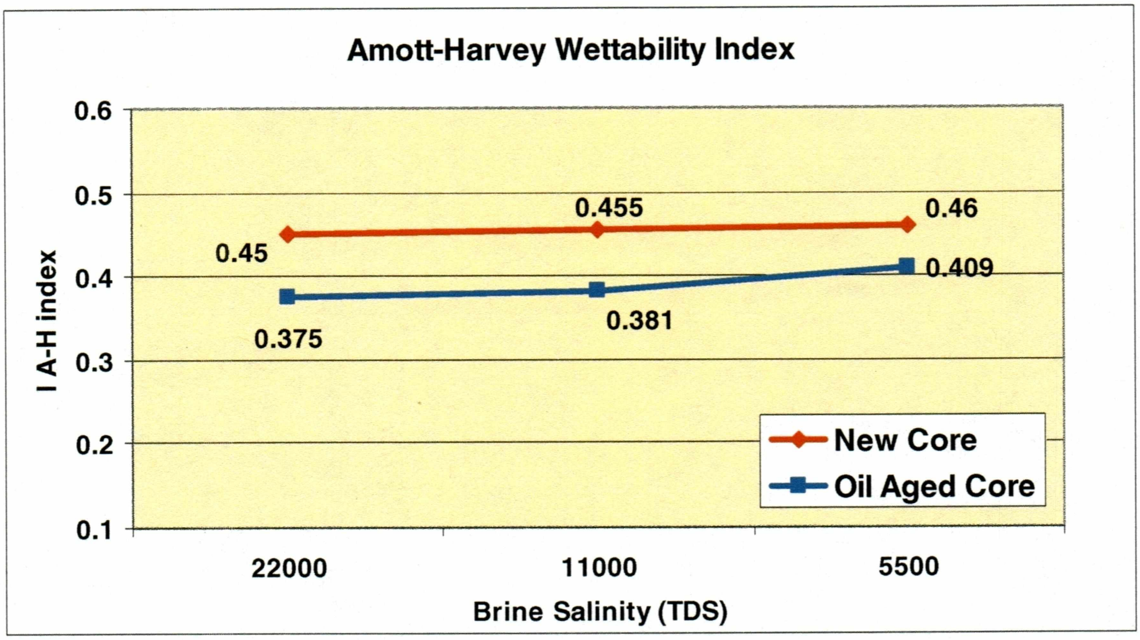

Figure A.8 Effect of Brine Salinity on Wettability (Core C)

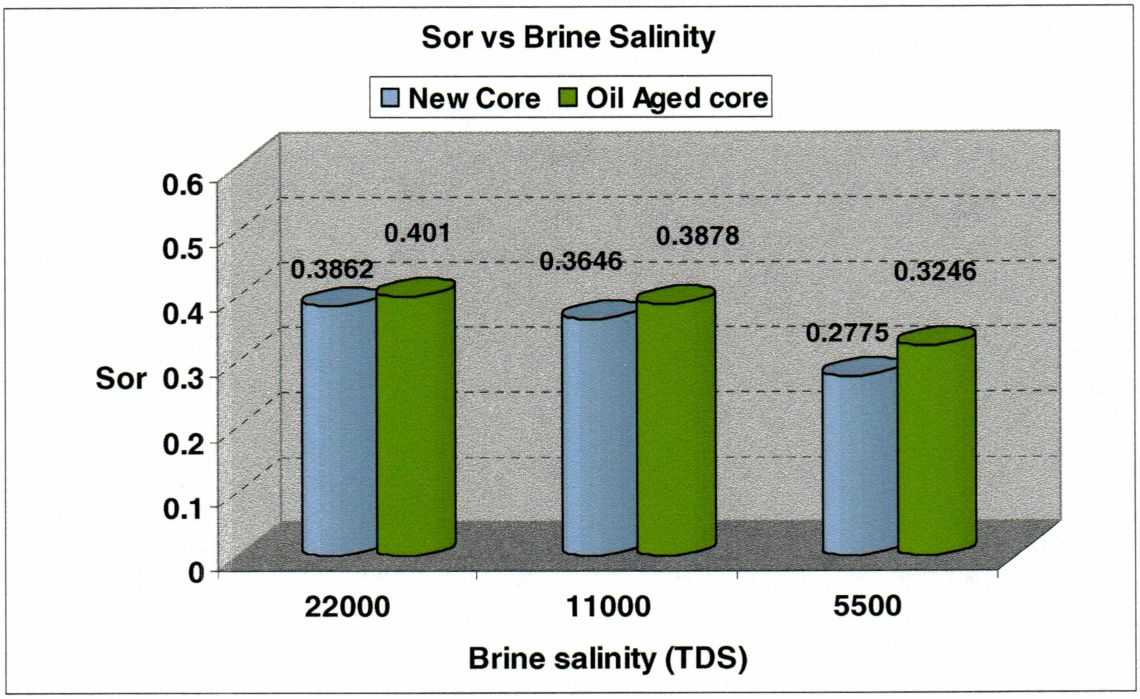

Figure A.9 Effect of Brine Salinity on Residual Oil Saturation (Core C)

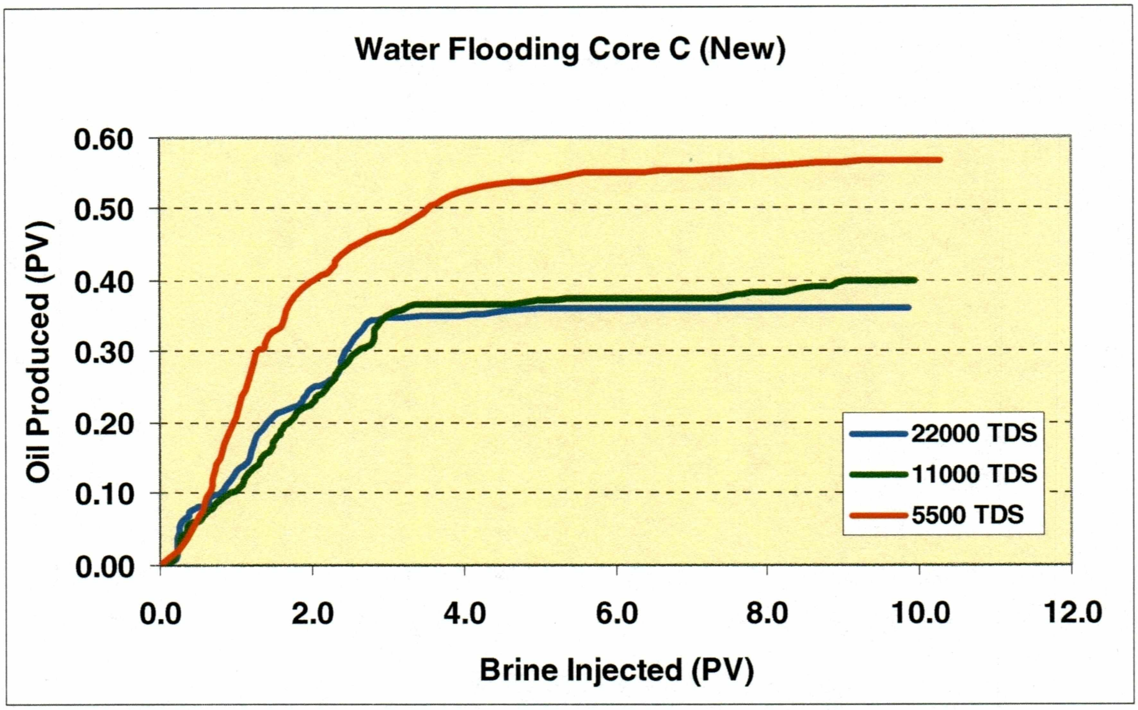

Figure A.10 Oil Recovery Profile for New Core C

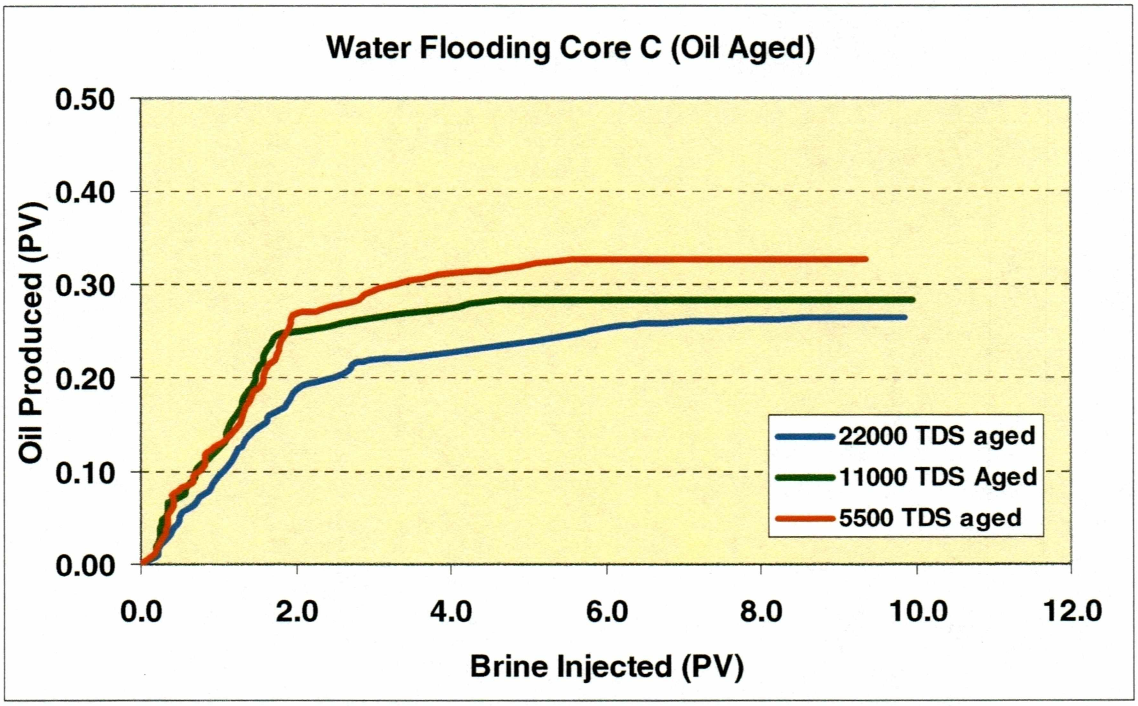

Figure A.11 Oil Recovery Profile for Oil Aged Core C

4) Core D

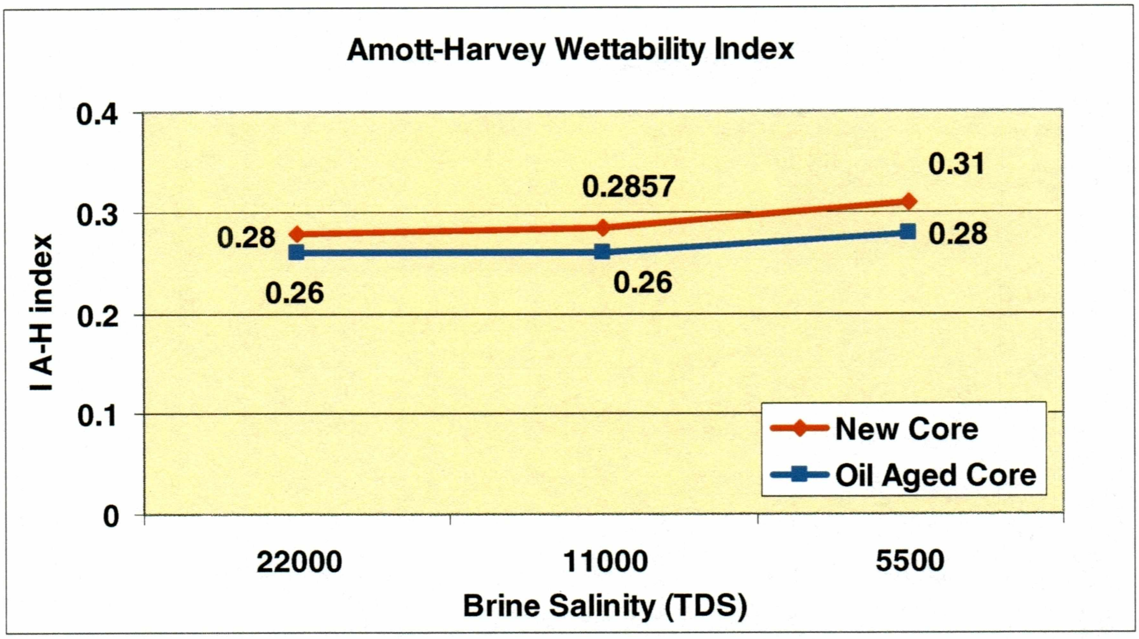

Figure A.12 Effect of Brine Salinity on Wettability (Core D)

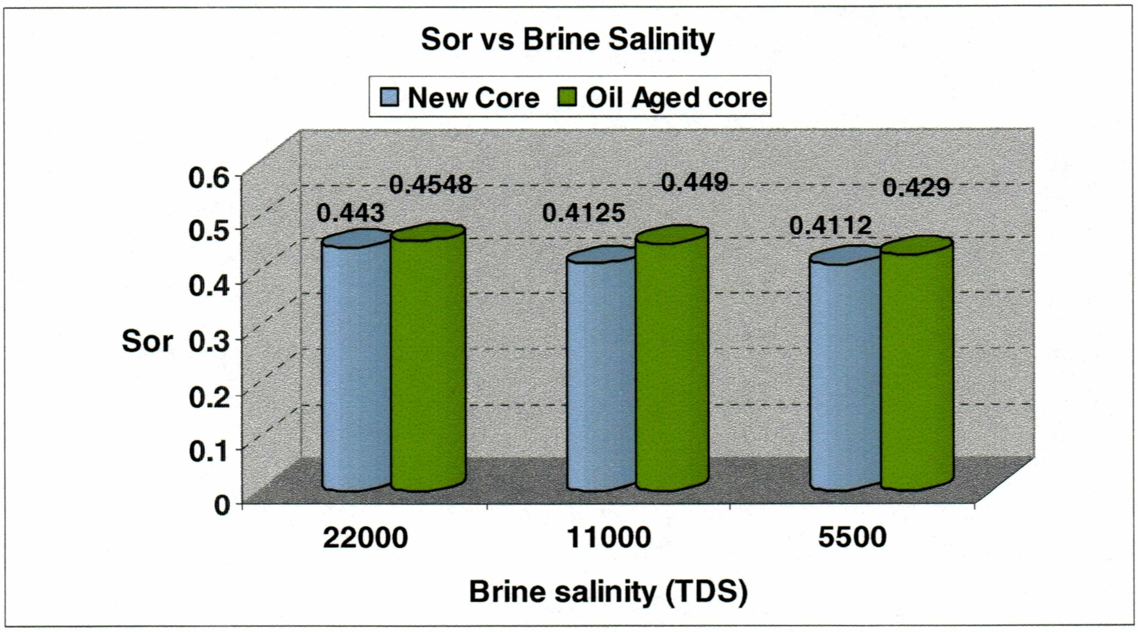

Figure A.13 Effect of Brine Salinity on Residual Oil Saturation (Core D)

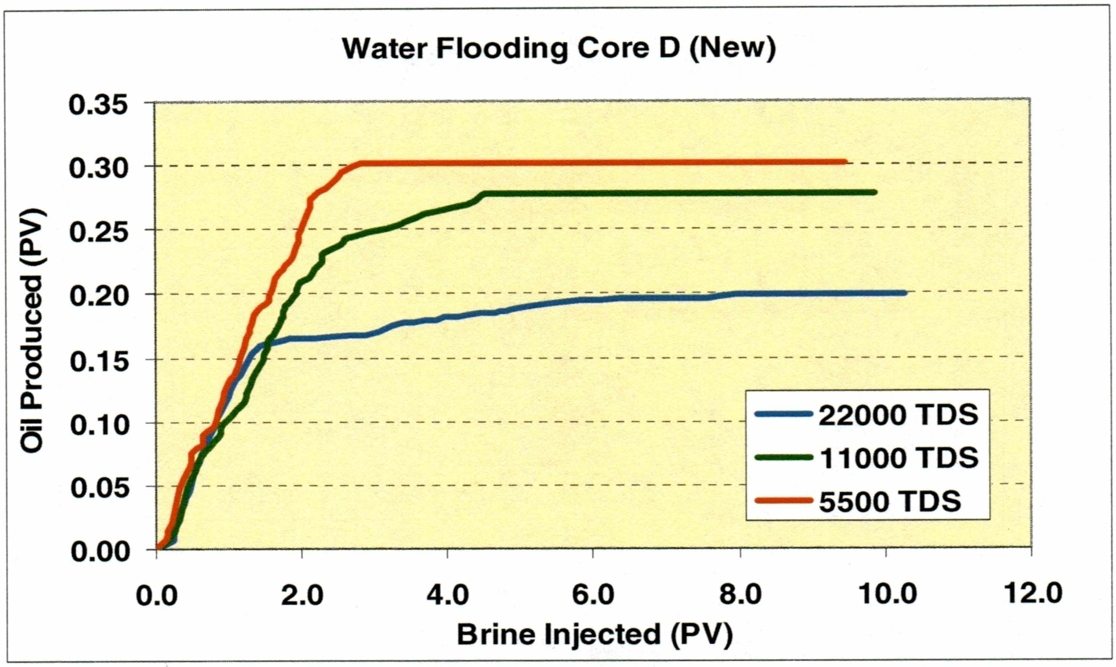

Figure A.14 Oil Recovery Profile for New Core D

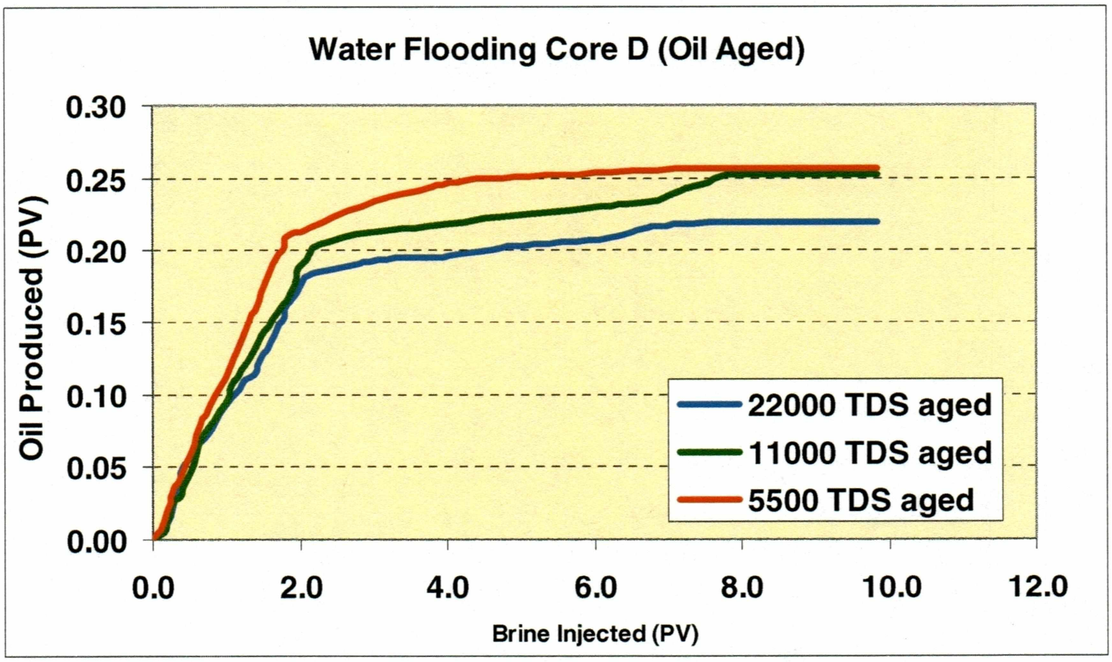

Figure A.15 Oil Recovery Profile for Oil Aged Core D

5) Core F

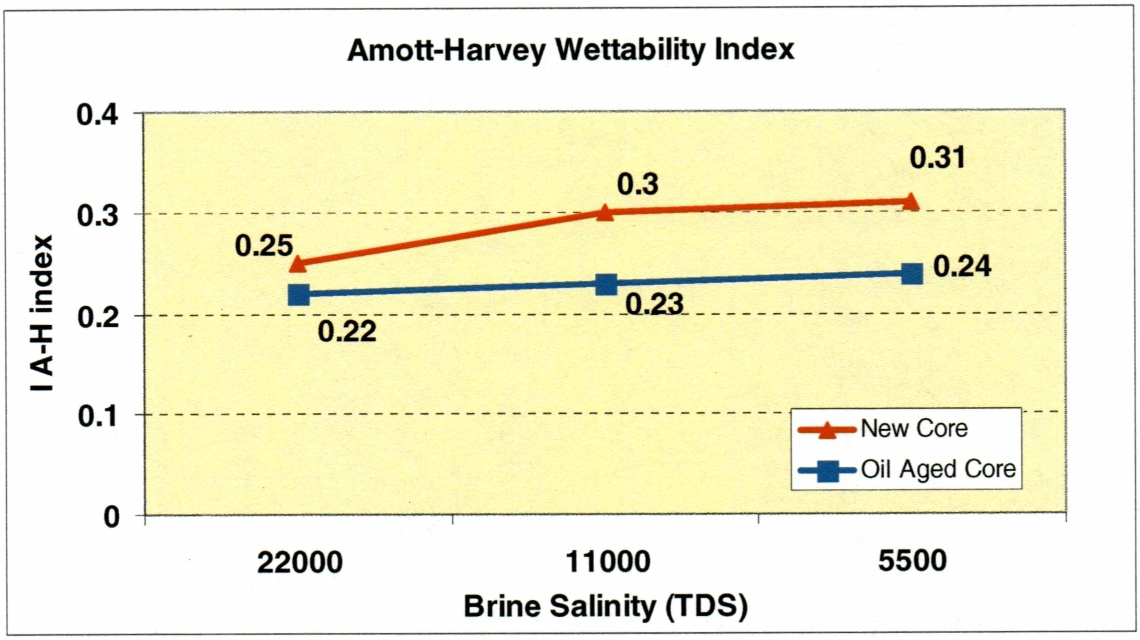

Figure A.16 Effect of Brine Salinity on Wettability (Core F)

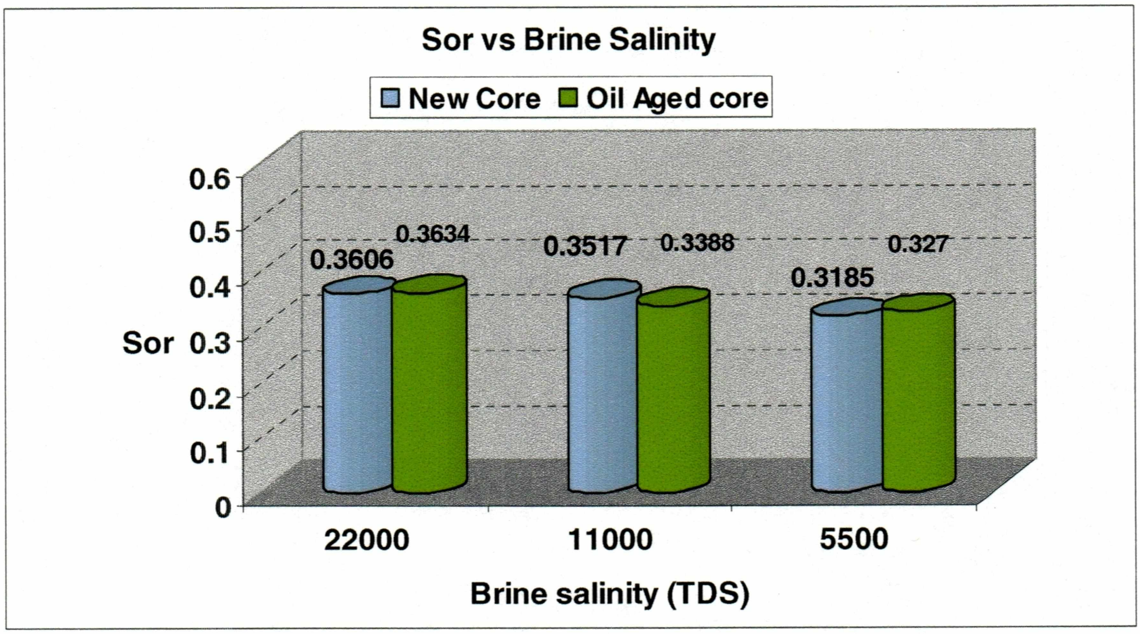

Figure A.17 Effect of Brine Salinity on Residual Oil Saturation (Core F)

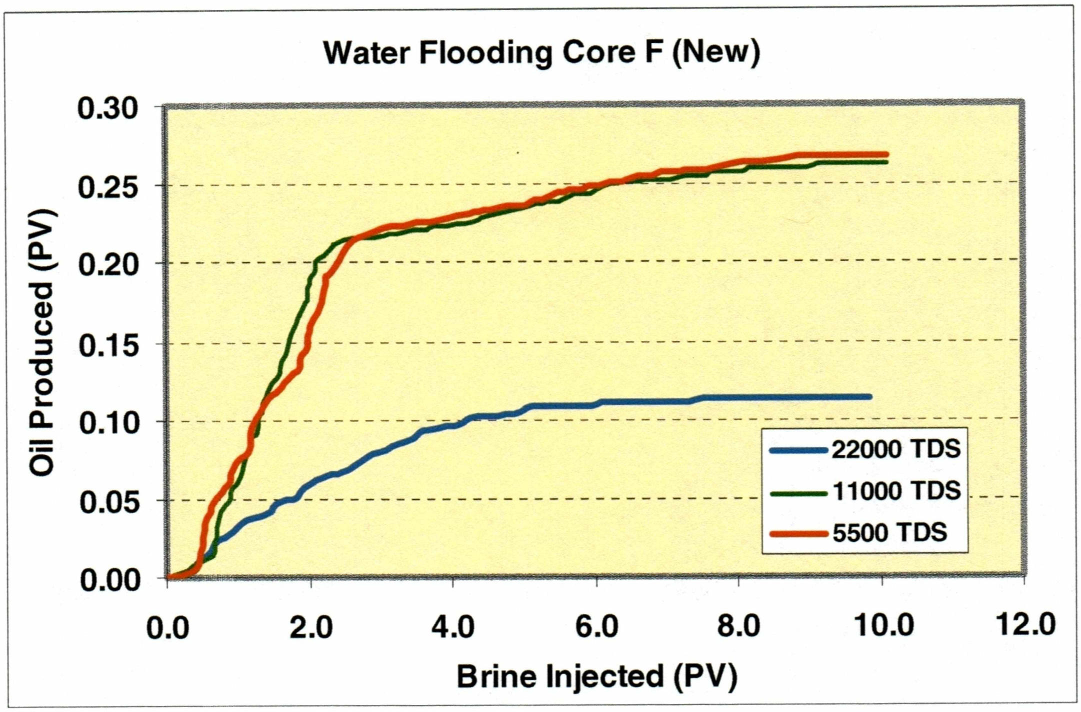

Figure A.18 Oil Recovery Profile for New Core F

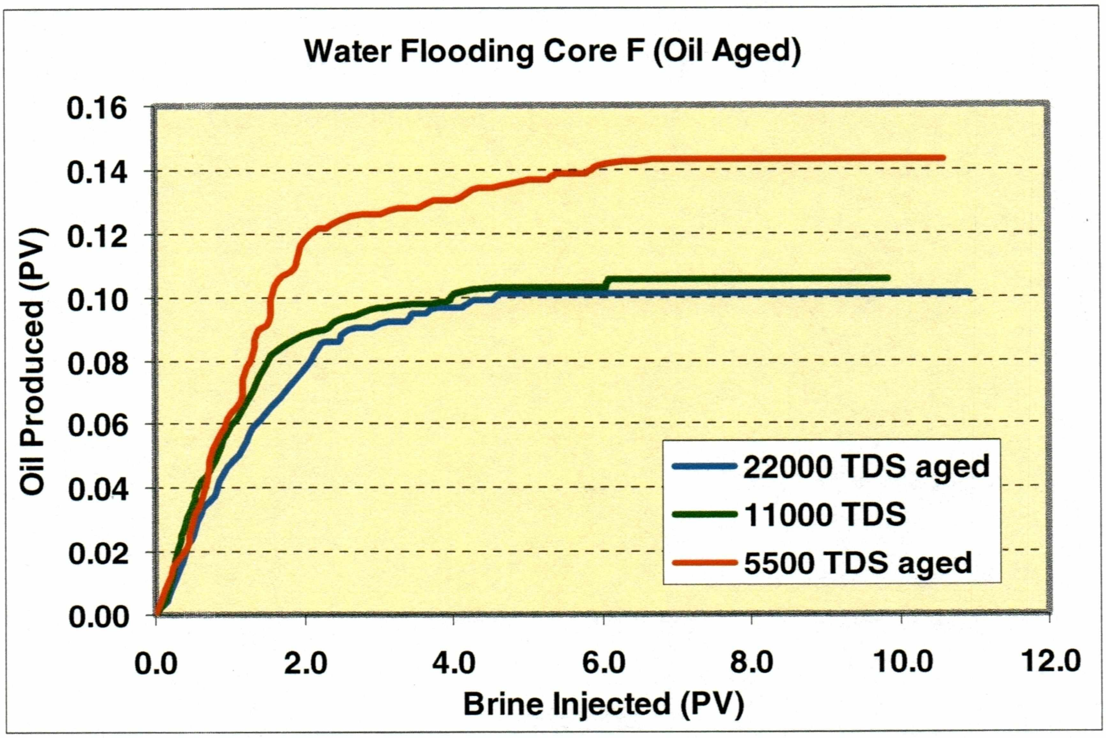

Figure A.19 Oil Recovery Profile for Oil Aged Core F

6) Core G

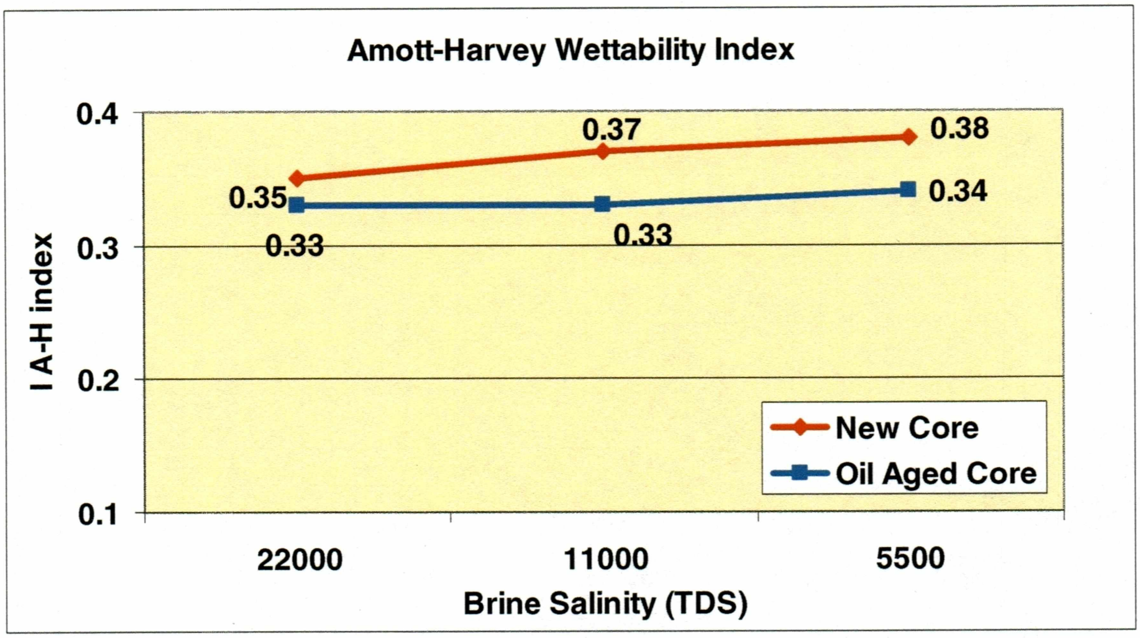

Figure A.20 Effect of Brine Salinity on Wettability (Core G)

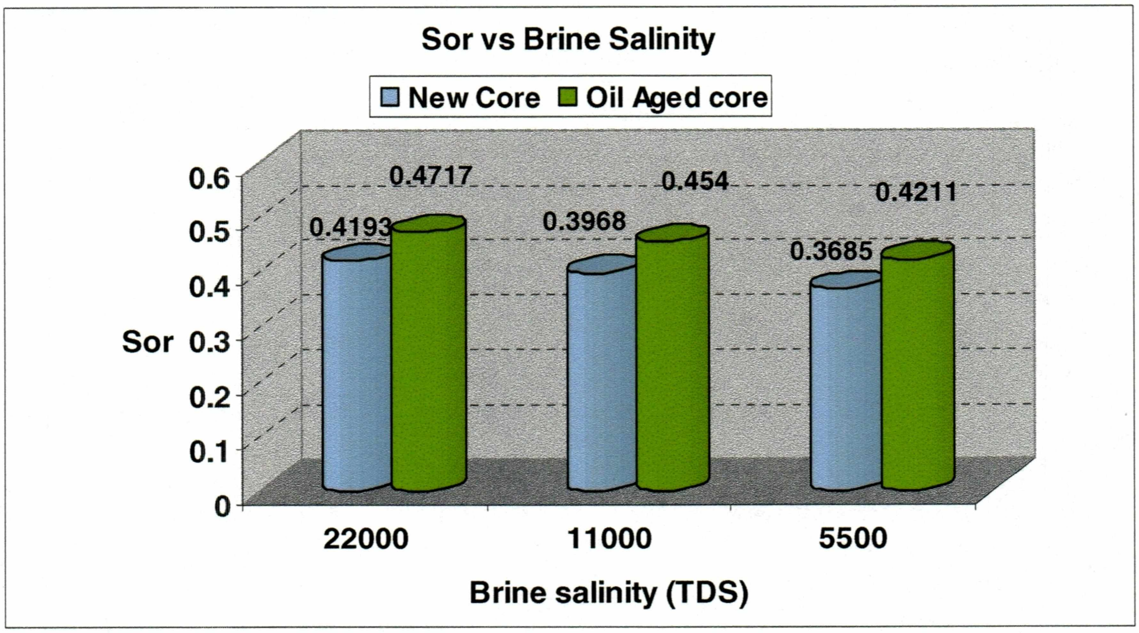

Figure A.21 Effect of Brine Salinity on Residual Oil Saturation (Core G)

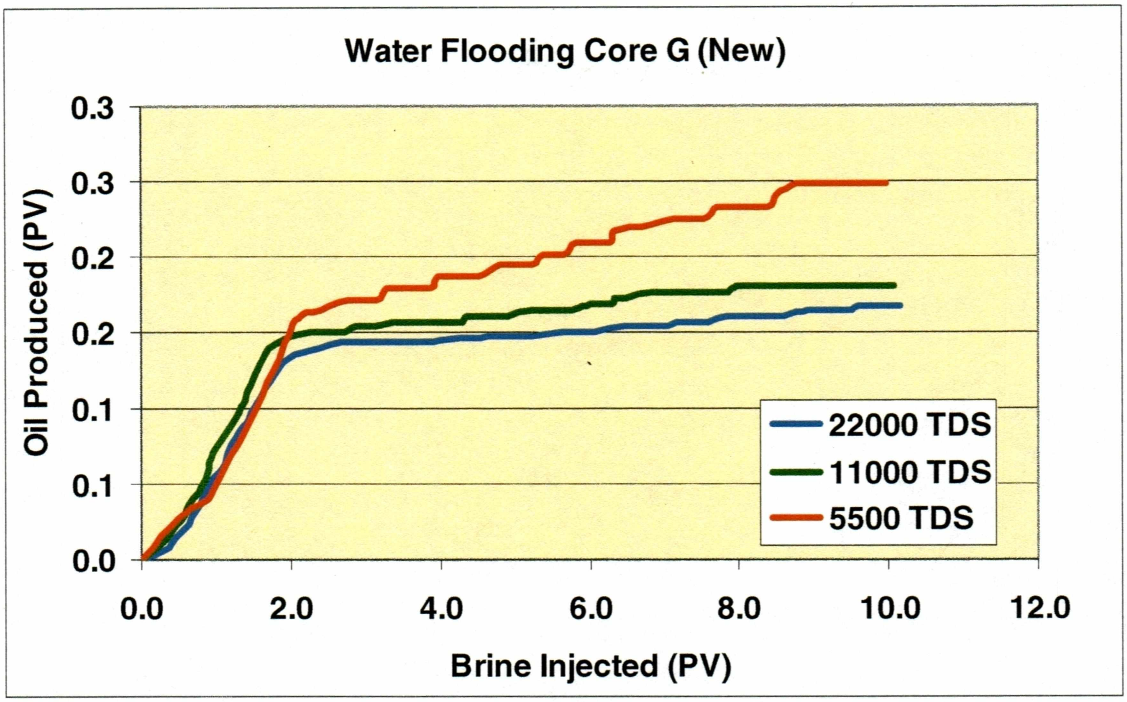

Figure A.22 Oil Recovery Profile for New Core G

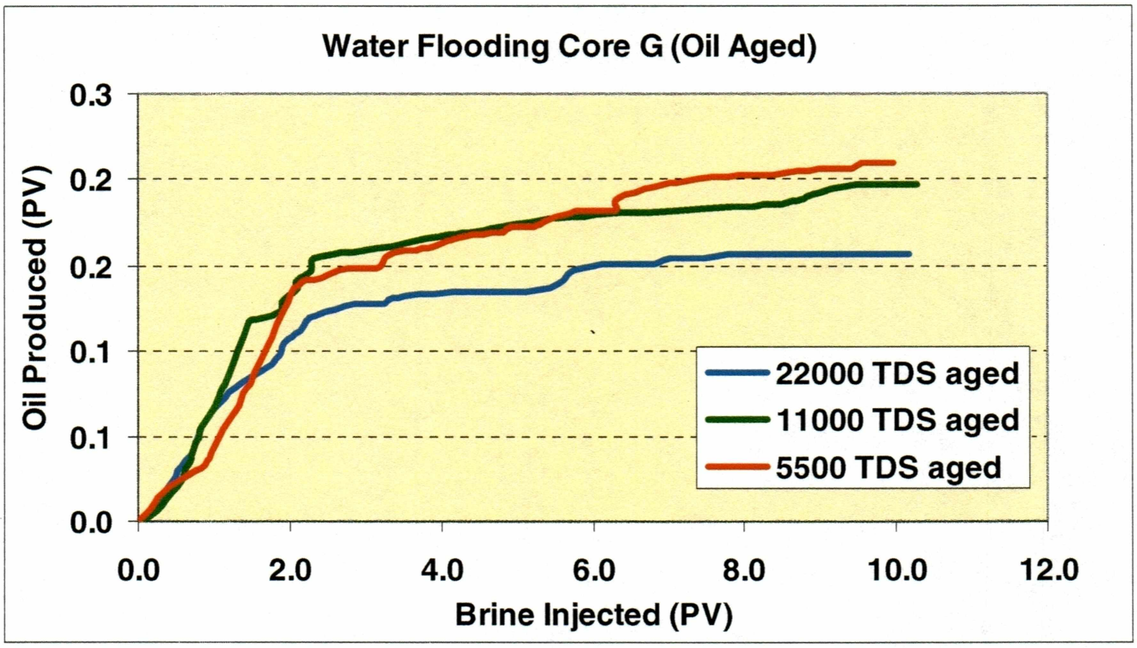

Figure A.23 Oil Recovery Profile for Oil Aged Core G

7) Core I

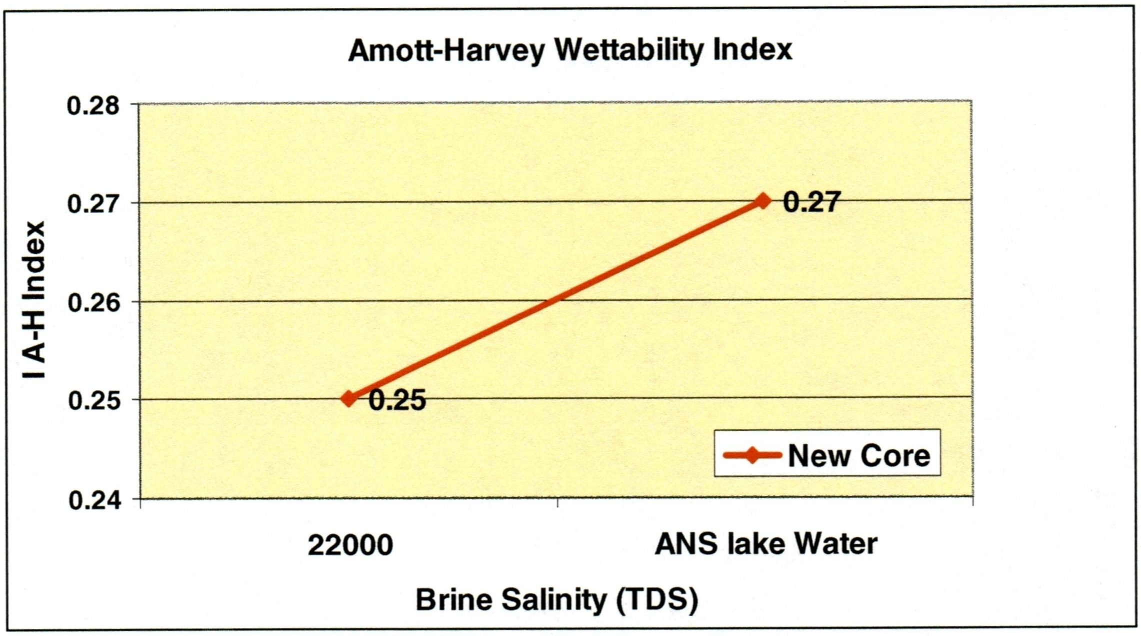

Figure A.24 Effect of Brine Salinity on Wettability for New Core I

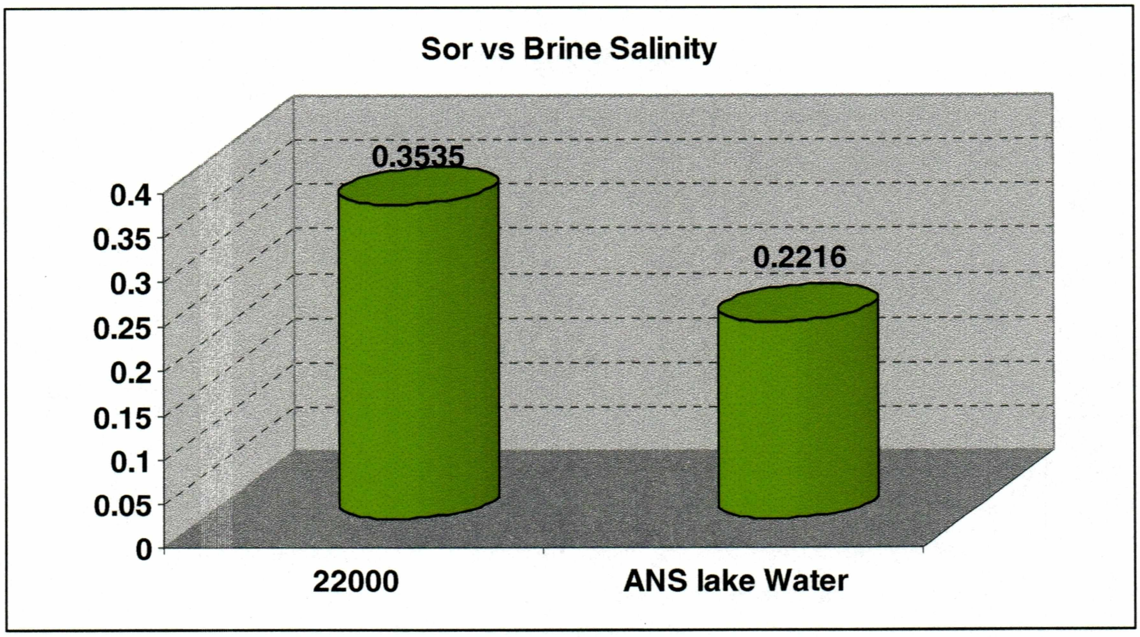

Figure A.25 Effect of Brine Salinity on Residual Oil Saturation for New Core I

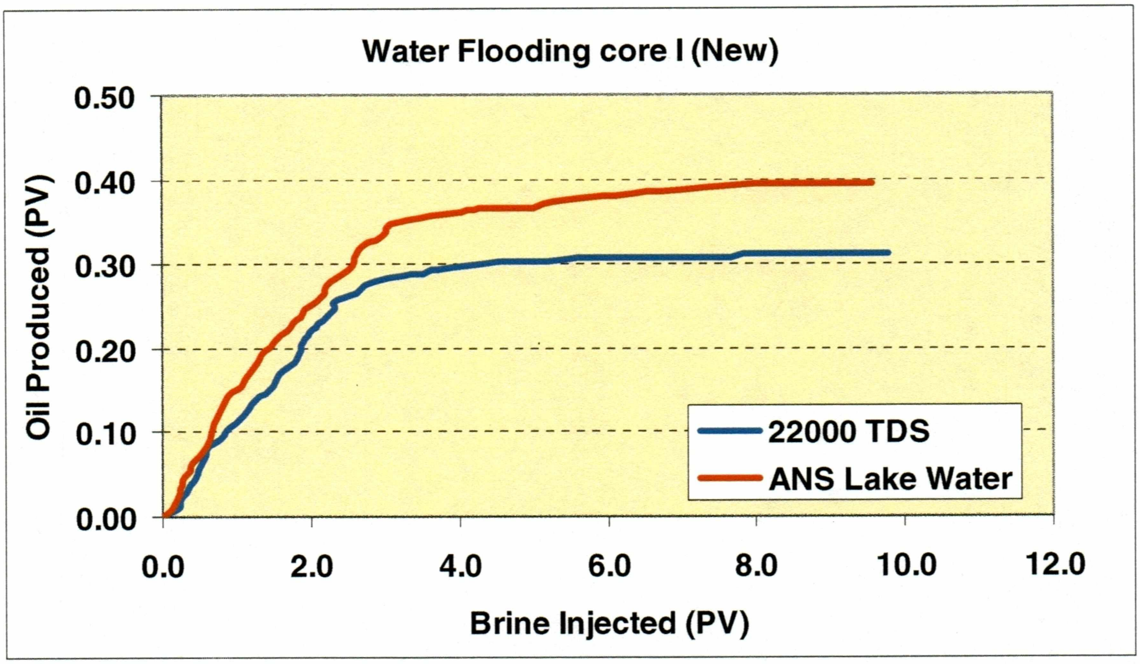

Figure A.26 Oil Recovery Profile for New Core I

8) Core J

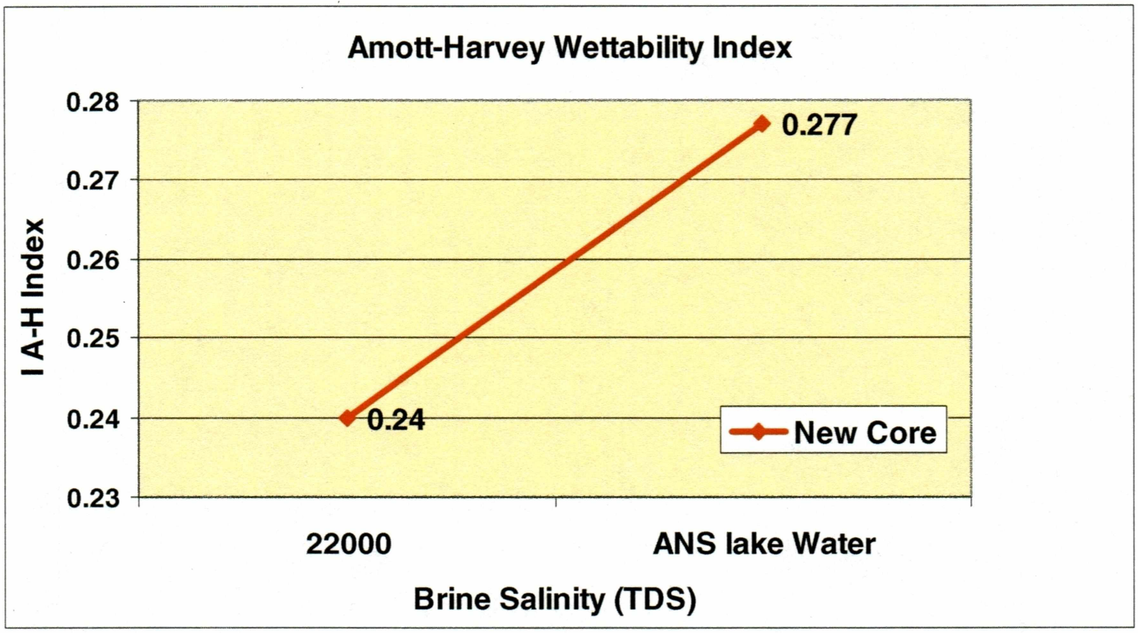

Figure A.27 Effect of Brine Salinity on Wettability for New Core J

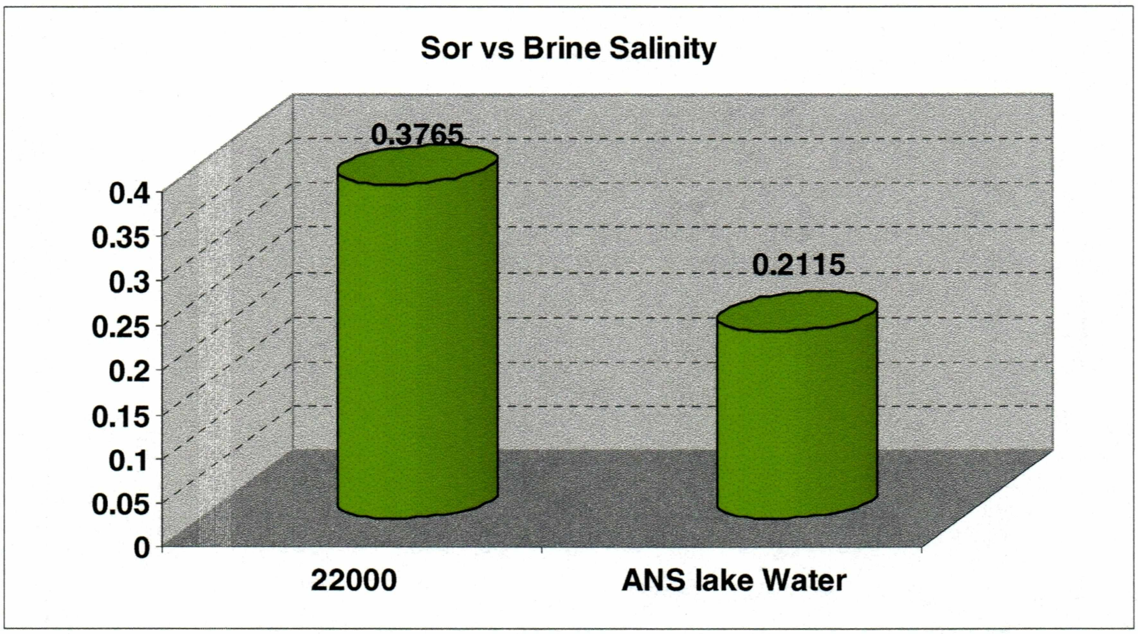

Figure A.28 Effect of Brine Salinity on Residual Oil Saturation for New Core J

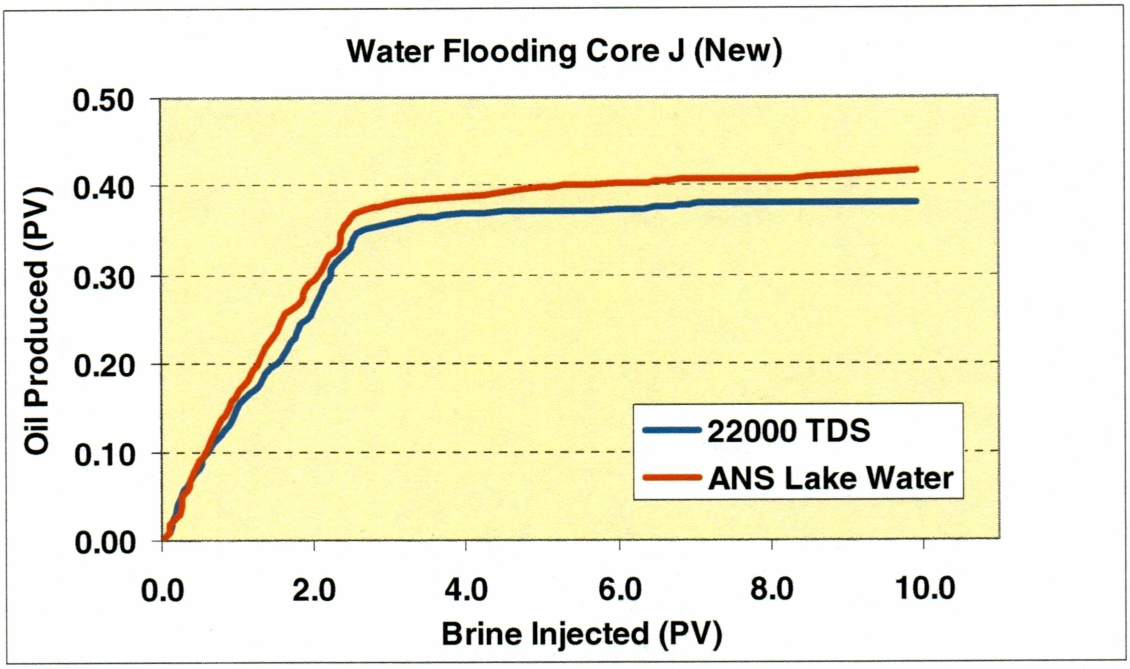

Figure A.29 Oil Recovery Profile for New Core J

Results of all the core samples are tabulated in the following table.

Table A.1 Results of Core Samples (A through G) Using Laboratory Brine

Core Name	**Unaged (New) Core Experiment Results**			**Aged Core Experiment Results**		
	22000 TDS	11000 TDS	5500 TDS	22000 TDS	11000 TDS	5500 TDS
A						
S_{or}	0.3959	0.2033	0.1986	0.4456	0.4239	0.4131
I_{AH}	0.4483	0.45	0.4545	0.375	0.3684	0.381
B						
S_{or}	0.3751	0.3011	0.297	Core got damaged		
I_{AH}	0.35	0.36	0.38	Hence no results		
C						
S_{or}	0.3862	0.3646	0.2775	0.401	0.3878	0.3246
I_{AH}	0.45	0.455	0.46	0.375	0.381	0.409
D						
S_{or}	0.443	0.4125	0.4112	0.4548	0.449	0.429
I_{AH}	0.28	0.2857	0.31	0.26	0.26	0.28
E						
S_{or}	0.4077	0.3837	0.3218	0.4631	0.4336	0.3857
I_{AH}	0.32	0.33	0.35	0.26	0.2683	0.282
F						
S_{or}	0.3606	0.3517	0.3185	0.3634	0.3388	0.327
I_{AH}	0.25	0.3	0.31	0.22	0.23	0.24
G						
S_{or}	0.4193	0.3968	0.3685	0.4717	0.454	0.4211
I_{AH}	0.35	0.37	0.38	0.33	0.33	0.34

Table A.2 Results of Core Samples (H through J) Using ANS Lake Water

Core Name	**22000 TDS**	**ANS lake Water**
H		
S_{or}	0.3971	0.2052
I_{AH}	0.26	0.29
I		
S_{or}	0.3535	0.2216
I_{AH}	0.25	0.27
J		
S_{or}	0.3765	0.2115
I_{AH}	0.24	0.277